are classified into +I & -I groups.

Atoms / groups which can withdraw $e^{\ominus}$ from carbon chain is called as '-I' groups.

-I group:

* $NR_3^+ > NF_3^+ > NH_3^+ > CF_3 > NO_2 > SO_2R >$

$-CN > -\overset{O}{\overset{\|}{C}}-H > -\overset{O}{\overset{\|}{C}}- > -\overset{O}{\overset{\|}{C}}-OH > -\overset{O}{\overset{\|}{C}}-OR >$

$-\overset{O}{\overset{\|}{C}}-NH_2 > CCl_3 > F > Cl > Br > I >$

Oph (OC_6H_5) > OR > -OH > $-NH_2$ > -ph >

$-C\equiv CH > -CH=CH_2 > H > D > T$

Atoms / groups which can donate electrons to carbon chain are called as '+I' groups.

+I group:

$\ddot{O}^- > S^- > -COO^- > R_3C > R_2CH- > R-CH_2- > -R >$

$T > D > H$

Applications of inductive effect:

① Stability of carbo cation (C^+) α +I groups

$CH_3^{\oplus} < CH_3-CH_2^{\oplus} < CH_3-CH^{\oplus}-CH_3$ α $\frac{1}{\text{-I groups}}$

$< CH_3-C^{\oplus}(CH_3)-CH_3$ (Stability)

[Magnitude of '+' charge] (E.N. α '-I') Stability ↓

Stability: $CH_3-\overset{\oplus}{C}H_2$ (sp^3) > $CH_2=\overset{\oplus}{C}H$ (sp^2) > $HC\equiv C^{\oplus}$ (sp)

EN: $sp > sp^2 > sp^3$

Stability : $CH_3^{\oplus} < CD_3^{\oplus} < CT_3^{\oplus}$

Stability : $\underset{-I}{NR_3}-CH_2-\overset{\oplus}{CH_2} < \underset{-I}{NH_3}-CH_2-\overset{\oplus}{CH_2}$

$< \underset{-I}{O_2N}-CH_2-\overset{\oplus}{CH_2}$

'+' ↑ : stability ↓

② Stability of carbanion ($C^{\ominus}$) α – I groups

Stability : α $\frac{1}{+I}$ groups

$CH_3^{\ominus} > \underset{+I}{CH_3}-\overset{\ominus}{CH_2}\ (1^{\circ}) > \underset{+I}{CH_3}-\overset{\ominus}{CH}-\underset{+I}{CH_3}\ (2^{\circ}) > \underset{+I}{CH_3}-\overset{\ominus}{\underset{\underset{+I}{CH_3}}{C}}-CH_3\ (3^{\circ})$

Stability : $CH_3-\overset{\ominus}{CH_2} < CH_2=\overset{\ominus}{CH} < HC\equiv C^{\ominus}$

sp^3 sp^2 sp

[EN α -I]

Stability : $CH_3^{\ominus} > CD_3^{\ominus} > CT_3^{\ominus}$

Stability : $H-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{CH_2} < NC-\overset{\ominus}{CH_2} < O_2N-CH_2^{\ominus}$

$\underset{-I}{}$ $\underset{-I}{}$ $\underset{-I}{}$

③ Acidic strength of carboxylic acids :

α -I groups

$HCOOH > \underset{+I}{CH_3}COOH > \underset{+I}{CH_3CH_2}COOH$

α 1/+I groups

Size of alkyl group ↑ $e^{\ominus}$ releasing tendency ↑

$CH_2(F)-COOH > CH_2(Cl)-COOH > CH_2(Br)-COOH > CH_2(I)-COOH$

(-I) (-I) (-I) (-I)

$CH_3-CH_2-\underset{Cl}{CH}-COOH > CH_3-\underset{Cl}{CH}-CH_2-COOH > CH_2(Cl)-CH_2-CH_2-COOH$

(-I) (-I) (-I)

④ Acidic strength of alcohols: $\alpha \frac{1}{+I \text{ groups}}$

Acidic : $\underset{(+I)}{CH_3OH} > \underset{(+I)}{CH_3CH_2OH}$

Acidic : $CH_3-OH > \underset{(-I)}{CH_2Cl-OH} > \underset{(-I)}{CH_2Br-OH} > \underset{(-I)}{CH_2I-OH}$

Acidic : $\underset{(-I)}{CH_2F-OH} < \underset{(-I)}{CHF_2-OH} < \underset{(-I)}{CF_3-OH}$

⑤ Dipole moment : α -I groups : $\alpha \frac{1}{+I \text{ groups}}$

μ : $\underset{-I}{CH_3Br} < \underset{-I}{CH_3Cl}$

⑥ Basic strength of amines : α +I group $\alpha \frac{1}{-I \text{ group}}$

$\underset{(+I)}{CH_3NH_2} > NH_3 > \underset{(-I)}{Ph-NH_2}$

(methyl amine) (Aniline)

Resonance / Delocalisation of $e^{\ominus}$:

To show resonance, compound must be in conjugation. (Alternate double bonds)

Eg : $CH_2 = \overset{\curvearrowright}{CH} - \overset{\curvearrowright}{CH} = CH_2 \leftrightarrow \overset{\oplus}{C}H_2 - CH = CH - \overset{\ominus}{C}H_2$

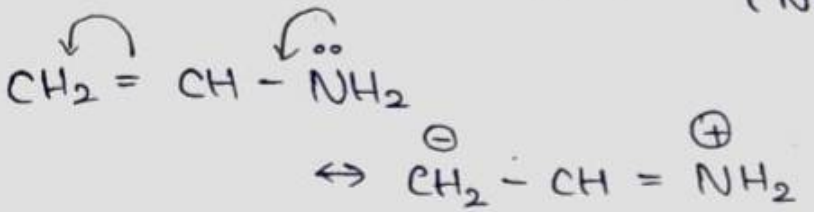
$CH_2 = \overset{\curvearrowright}{CH} - \overset{O}{\overset{\|}{C}} - H \leftrightarrow \overset{\oplus}{C}H_2 - CH = \overset{O^{\ominus}}{\overset{|}{C}} - H$

$CH_2 = \overset{\curvearrowright}{CH} - \overset{O}{\overset{\|}{C}} - OH \leftrightarrow \overset{\oplus}{C}H_2 - CH = \overset{O^{\ominus}}{\overset{|}{C}} - OH$

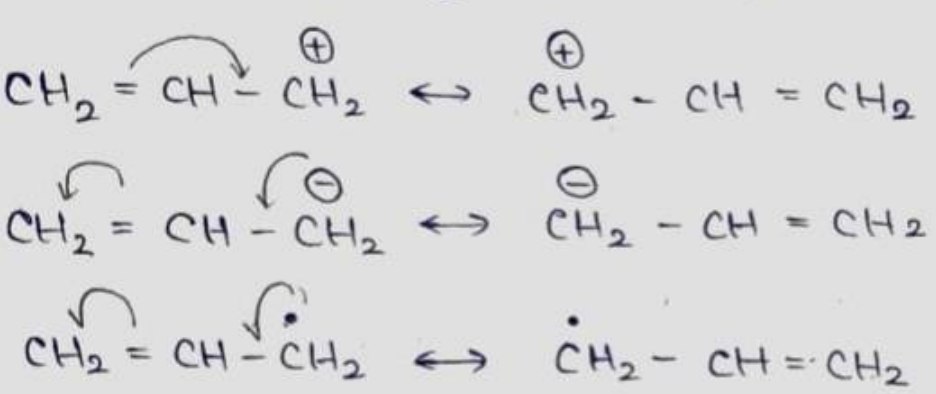
$CH_2 = CH - N\overset{O}{\underset{O}{<}} \leftrightarrow \overset{\oplus}{C}H_2 - CH = N\overset{O^{\ominus}}{\underset{O}{>}}$

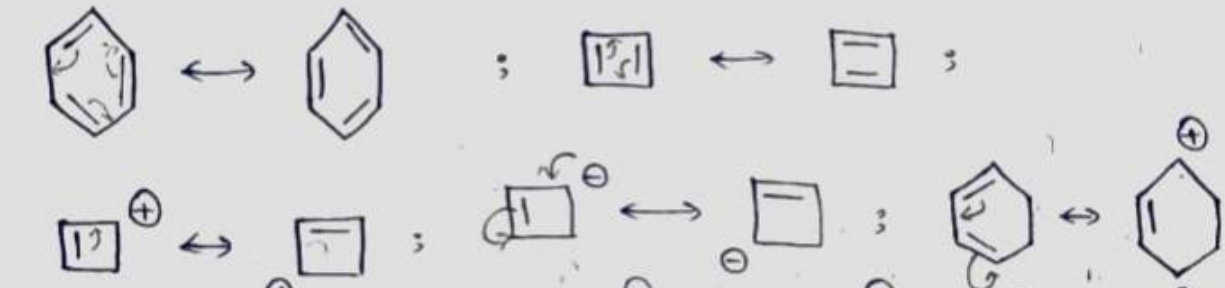
$CH_2 = CH - FG$ ✓ (Lone-pair on functional group)

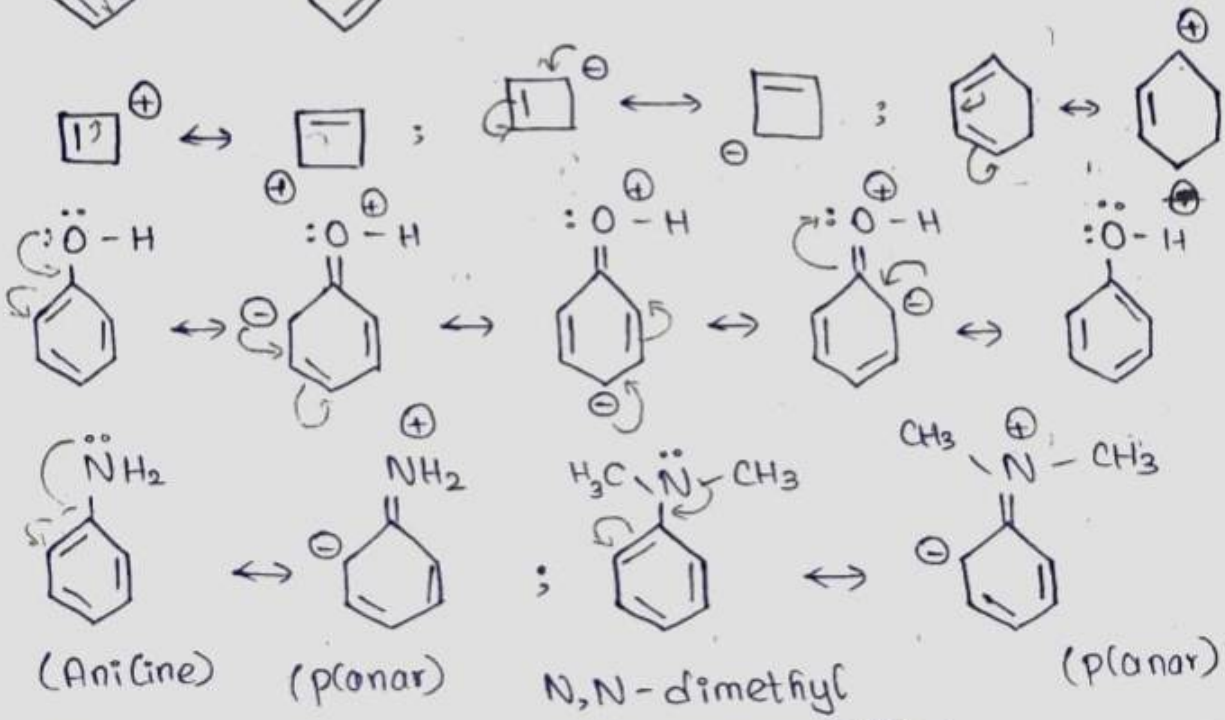
(Non-bonding $e^{\ominus}$ initiates first)

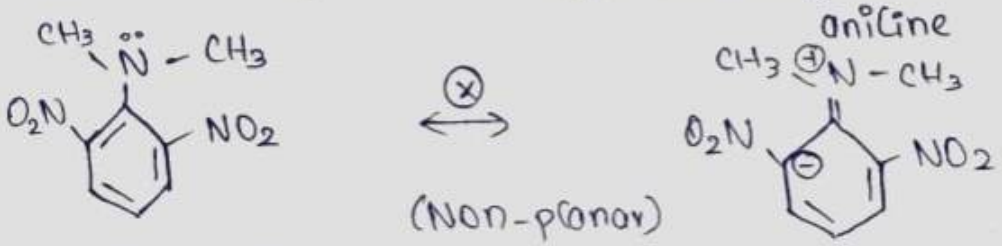


(-) → 1 lone pair



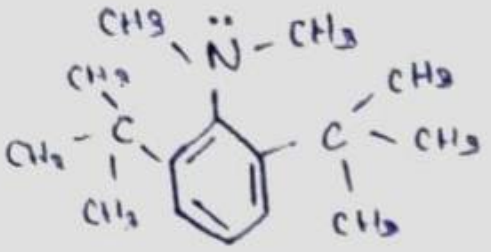






Steric strain

Steric Inhibition of resonance effect



(Non-planar)

(Bulky groups present at ortho positions) ↓ compounds not involved in resonance

$$CH_2 = CH - CH = CH_2 \longleftrightarrow \overset{\oplus}{C}H_2 - CH = CH - \overset{\ominus}{C}H_2$$

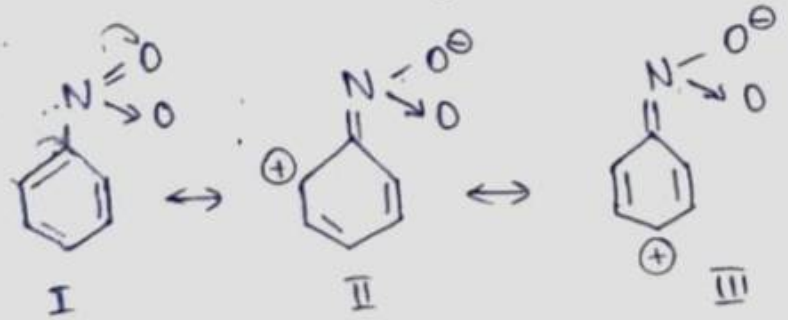
(I) (II)

Stability : I > II

Stability :

$$CH_2 = CH - N(=O)-O \;>\; \overset{+}{C}H_2 - \overset{-}{C}H - \overset{+}{N}(=O)-O^{\ominus} \;>$$

$$\overset{\ominus}{C}H_2 - \overset{\oplus}{C}H - \overset{\oplus}{N}(=O)-O^{\ominus}$$



I II III

Stability : I > II > III

$$\overset{\backslash}{\underset{/}{C}}=\ddot{O}: \;>\; \overset{\backslash}{\underset{/}{C}}-\overset{\oplus}{O}^{\ominus} \;>\; \overset{\backslash}{\underset{/}{C}}^{\ominus}-O^{\oplus}$$

I II III

* No. of covalent bonds must be more
* More EN atom → '−' charge
  Less EN atom → '+' charge
* Distance b/w charge ↑ Stability ↓

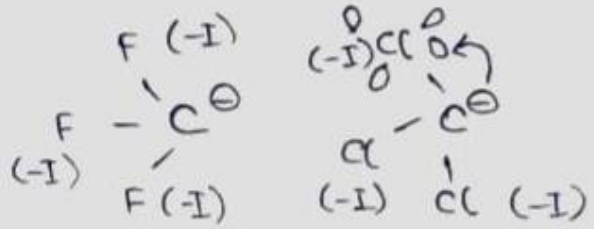
(Stability) → Because of aromatic nature

Aromatic nature : → cyclic, planar (sp^2)

$(4n+2)\pi e^{\ominus} \Rightarrow 2\pi e^{\ominus}$

$n = 0, 1, 2, \ldots$

Stability : $CF_3^{\ominus} < CCl_3^{\ominus}$ (d-orbital resonance)

 (back-bonding)

Stability : $CF_3 - CH_2^{\ominus} > CCl_3 - CH_2^{\ominus}$

(-I) (-I)

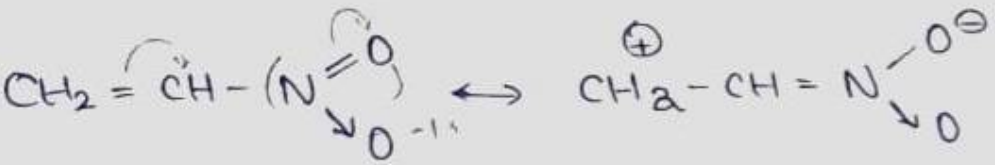
$CH_3 - CH_2 - CH_2^{\ominus}$, $CH_2 = CH - CH_2^{\ominus} \leftrightarrow$

sp^3 sp^3 sp^3 sp^2 sp^2 sp^2

$CH_2^{\ominus} - CH = CH_2$

sp^2

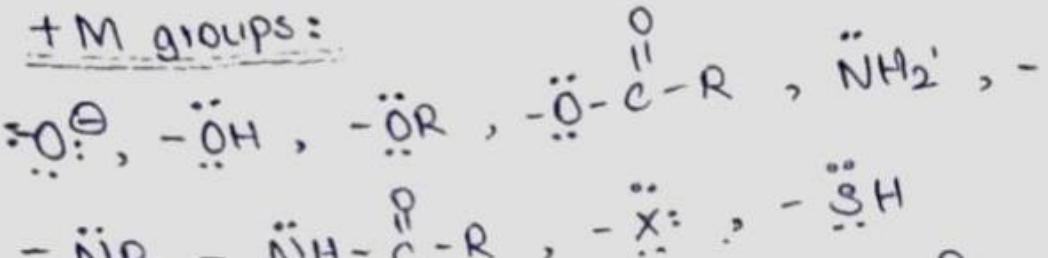
Mesomeric effect (M) :



Delocalization of non-bonding / π-bonding electrons in a conjugated system is called as mesomeric effect.

Based on mesomeric effect, atoms / groups are classified into two types : (+M) & (-M) groups

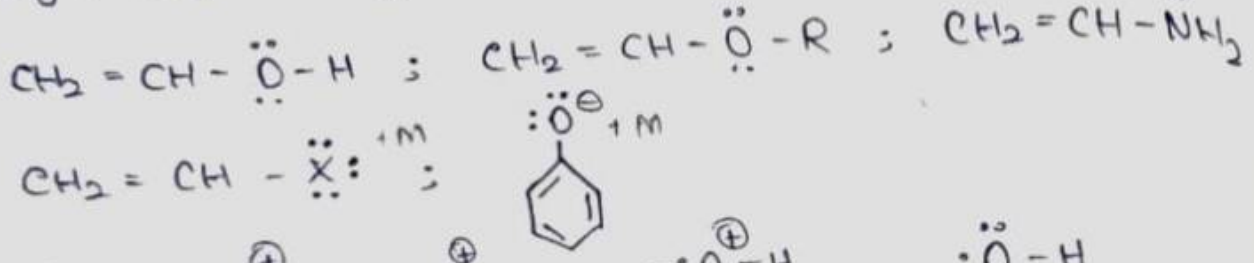
+M groups:

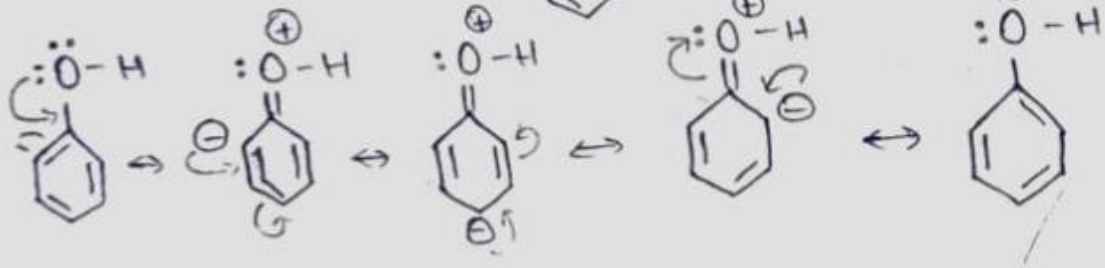


(∴) $-\ddot{O}^{\ominus} > -\ddot{N}H_2 > -\ddot{O}H > -\ddot{O}R > -\ddot{N}H-\overset{O}{\overset{\|}{C}}-R$

"+M" groups can donate electrons to conjugated system.

Eg: $CH_2=CH-\ddot{O}:$

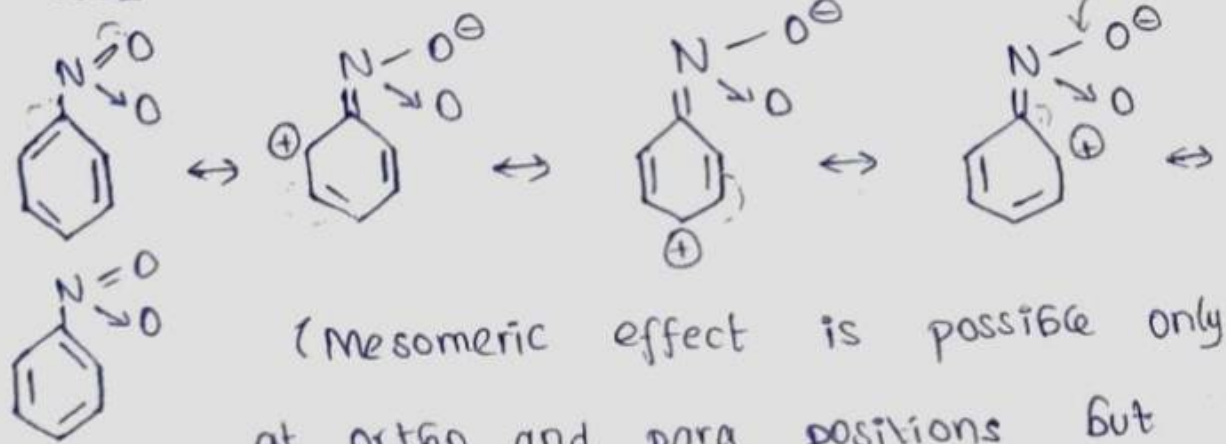




Atoms / groups which can withdraw $e^{\ominus}$ from conjugated system are known as '-M' groups.

-M groups:

$-NO_2 > -CN > -SO_3H > -\overset{O}{\overset{\|}{C}}-H > -\overset{O}{\overset{\|}{C}}-$



(Mesomeric effect is possible only at ortho and para positions but not at meta positions).

Stability : $CH_3-CH_2-CH_2^{\oplus}$ < $CH_2=CH-CH_2^{\oplus}$

Conjugation (M)

Stability of carbocation is mainly given by mesomeric effect.

Allyl carbocation

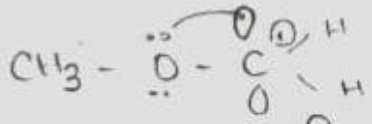
Stability : $CH_2=CH^{\oplus}$ < $CH_2=CH-CH_2^{\oplus}$

Vinyl carbocation — Allyl carbocation (conjugation / M)

Stability : $CH_2=CH-CH_2^{\oplus}$ < $ph-CH_2^{\oplus}$

Allyl carbocation (Conjugation / M) — Benzyl carbocation (conjugation (more) / M)

Stability : $CH_3-\ddot{O}-CH_2^{\oplus}$ > $CH_2=CH-CH_2^{\oplus}$



(lone pair back bonding)

Stability : $CH_3-\ddot{O}-CH_2^{\oplus}$ > $ph-CH_2^{\oplus}$

Stability : $CH_3-CH_2-\ddot{O}-CH_2^{\oplus}$ > $CH_3-\ddot{O}-CH_2-CH_2^{\oplus}$

Stability : $CH_3-CH_2-CH_2^{\ominus}$ < $CH_2=CH-CH_2^{\ominus}$

(+I)

Allyl carbanion (conjugation / M)

Stability : $CH_2=CH^{\ominus}$ < $CH_2=CH-CH_2^{\ominus}$

Vinyl carbanion — (conjugation / M)

Allyl carbanion

Stability: $CH_3-\overset{\oplus}{C}H-CH_3$ < $ph-\overset{\oplus}{C}H_2$

Alkyl carbonium — Benzyl carbonium

C-C Bond length: CH_3-CH_3 > $CH_3-CH=CH_2$ > $CH_2=CH-C\equiv CH$

Electromeric effect (E):

Shifting of π-bonding e$^\ominus$ in presence of attacking reagents (electrophile & nucleophile) is called as electromeric effect. It is of two types: +E & -E effect.

In +E effect shifting of π-bonding e$^\ominus$ can take place in presence of electrophile.

+E effect:

Eg: $CH_3-CH=CH_2 + H^\oplus \rightarrow CH_3-\overset{\oplus}{C}H-CH_3$ (Major, 2°) + $CH_3-CH_2-\overset{\oplus}{C}H_2$ (1°, Minor)

(Nucleophile) (Electrophile)

Shifting of π electrons in presence of nucleophile is called as -E effect.

-E effect:

Eg: $R-\overset{O}{\overset{\|}{C}}-H + (:)^\ominus \rightarrow R-\overset{O^\ominus}{\overset{|}{C}}-H$

(Nucleophile)

Note : Electromeric effect is possible in compounds having multiple bonds like

$-C=C-$, $-C\equiv C-$, $-\overset{O}{\overset{\|}{C}}-H$, $-\overset{O}{\overset{\|}{C}}-$,

$R-\overset{O}{\overset{\|}{C}}-OH$, $R-\overset{O}{\overset{\|}{C}}-NH_2$, $R-\overset{O}{\overset{\|}{C}}-OR$, $R-\overset{O}{\overset{\|}{C}}-Cl$

Inductomeric effect :

In presence of attacking reagents inductive effect phenomena increases which is called as inductomeric effect.

Eg : SN^2 (Bimolecular nucleophilic substitution)

$$\underset{(-I)}{CH_3-Cl} + \underset{(-I)}{OH^{\ominus}} \longrightarrow CH_3-OH + Cl^{\ominus}$$

(Attacking reagent)

Rd $[CH_3Cl][OH]^-$ (order = 2)

Stability : $< R-\overset{O}{\overset{\|}{C}}-O^{\ominus}$ Because of resonance equivalence

Aromatic :

planar, cyclic, $(4n+2)\pi\ e^{\ominus}$
(sp^2)

Anti-aromatic :

planar (sp^2), cyclic, $4n\pi\ e^{\ominus}$

Stability : Aromatic > Non-aromatic > Anti-aromatic

* Hyper conjugation / σ-π conjugation / No bond resonance / Baker-nathan effect :

Q) Which of the following can show hyperconjug. -ation :

i) $CH_2 = CH_2$ ii) $CH_3 - CH = CH_2$ iii) $CH_3 - CH = CH - CH_3$

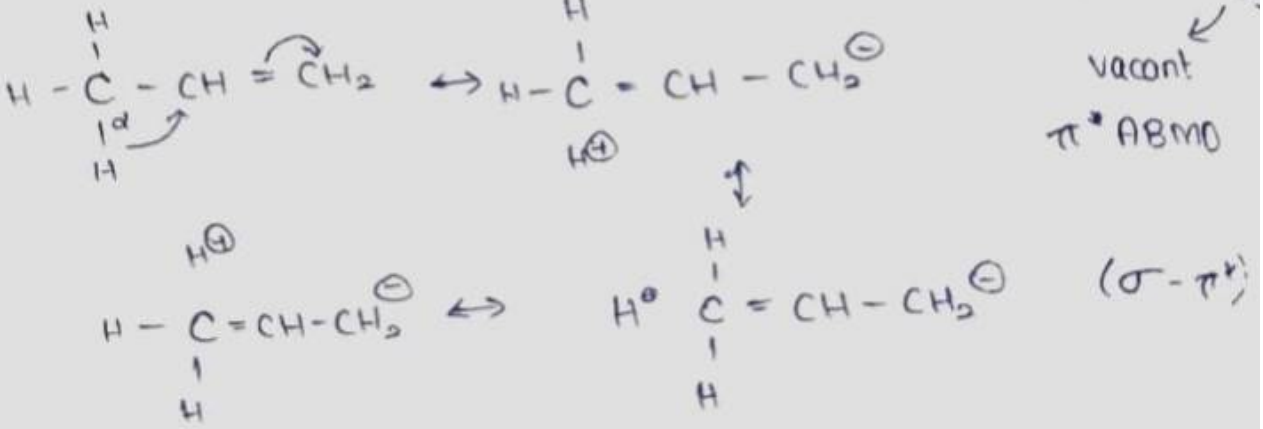
iv) $CH_3 - \overset{\oplus}{C}H_2$ v) $CH_3 - \dot{C}H_2$ vi) $CH_3 - \overset{O}{\overset{\|}{C}} - H$

vii) $CH_3 - CH_2 - OH$ viii) $CH_3 - COOH$

Hyperconjugation explains the stability of alkenes, carbocations and free-radicals but not carbanion and compounds containing other functional groups.

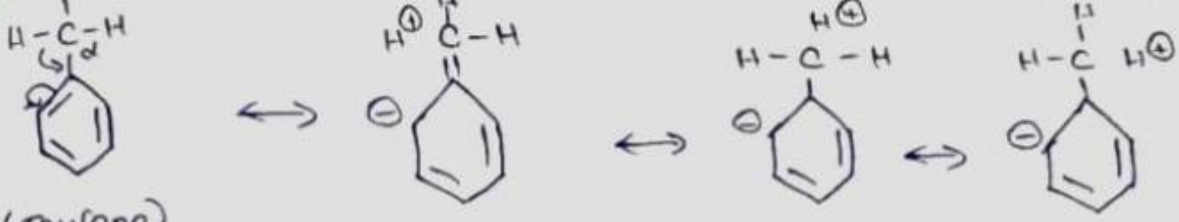
$CH_3 - CH = CH_2$ (d)

C_3 (12e$^\ominus$) : $\sigma_{1s}^2\ \sigma_{2s}^2\ \sigma_{2s}^2\ \sigma_{2s}^{*2}\ \pi_{2p_x}^2\ \pi_{2p_y}^2\ \pi^*_{2p}\ \pi'^*_{2p}$



Definition :

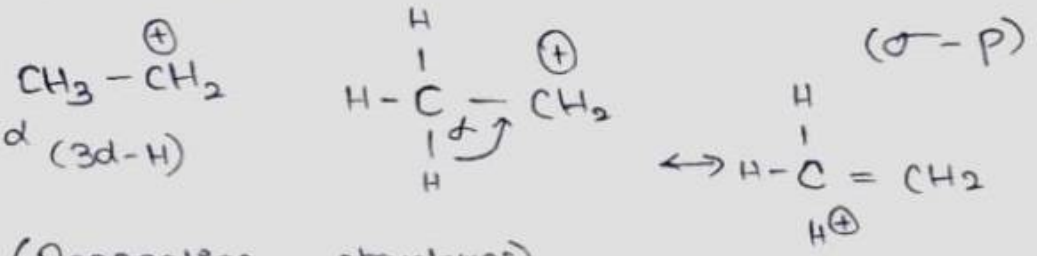
Shifting of α_{C-H} "σ" electrons to vacant π^* ABMO of carbon atom of adjacent π-bonded system is called as hyperconjugation



(Toulene)

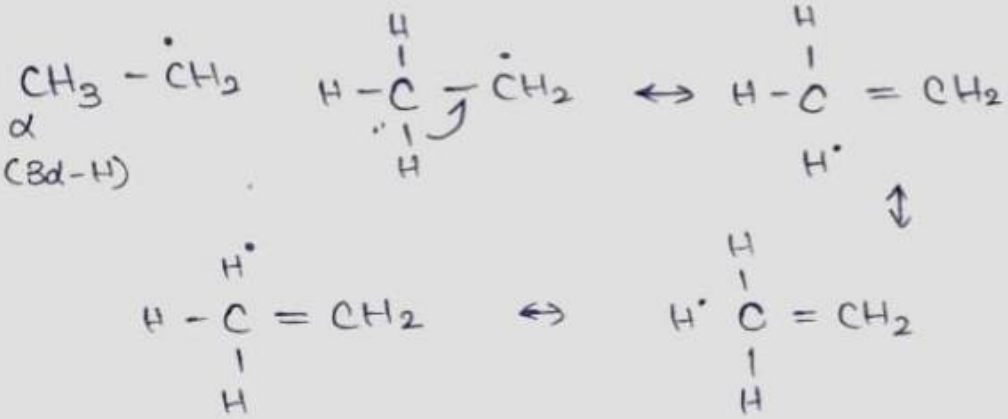
(Methyl Benzene)

* Hyper conjugation in carbocation :



(Resonating structures)

* Hyper conjugation in free-radicals :



Hyper conjugation explains stability of alkenes, carbo cation, free radical but not carbonion.

C^+ stability } I, M, HC

$C^\cdot$ stability } I, M, HC] → mostly

C^- stability } I, M, HC (x)

* Applications of hyper conjugation :

i) Stability of alkenes :

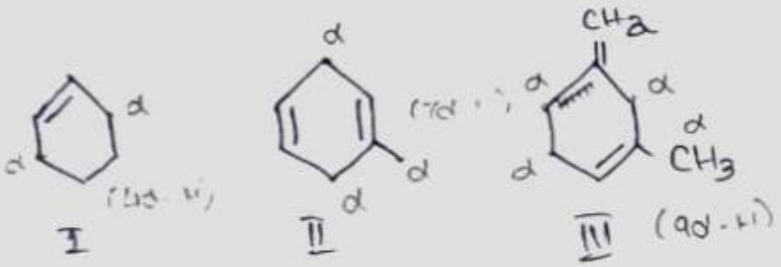
$CH_2 = CH_2$ (I) $\overset{\alpha}{C}H_3 - CH = CH_2$ (II) $\overset{\alpha}{C}H_3 - CH = CH - \overset{\alpha}{C}H_3$ (III)

(3α-H) (6α-H)

$CH_3 - \overset{\alpha CH_3}{\overset{|}{C}} = CH - \overset{\alpha}{C}H_3$ (IV) $H_3\overset{\alpha}{C} - \overset{\alpha CH_3}{\overset{|}{C}} = \overset{CH_3\alpha}{\overset{|}{C}} - \overset{\alpha}{C}H_3$ (V)

(9α-H) (12α-H)

Stability : I < II < III < IV < V



I II III (9α-H)

Stability : I < II < III

* Heat of hydrogenation :

Amount of energy released when an alkene undergoes hydrogenation is called as heat of hydrogenation.

Eg : $R - CH = CH_2 + H_2 \rightarrow R - CH_2 - CH_3$ $\Delta H = -ve$

* Heat of combustion :

Amount of energy released when one mole of an alkene undergoes combustion with excess of oxygen is called as heat of combustion.

Eg : $\underset{(Alkene)}{C_2H_4} + 3O_2 \rightarrow 2CO_2 + 2H_2O$ $\Delta H = -ve$

Stability $\propto \frac{1}{\text{Heat of hydrogenation / Heat of combustion}}$

(3α)
$CH_3 - \overset{\alpha}{CH} = CH_2$ I

$CH_3 - \overset{\alpha}{CH} = CH - \overset{\alpha}{CH_3}$ (6α) II

Stability : I < II

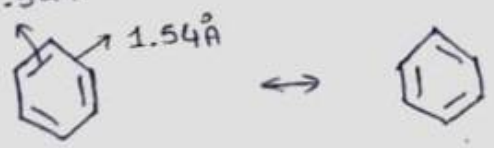
Heat of hydrogenation / Heat of combustion : I > II

ii) Bond - length :

a) $CH_3 - CH = CH_2$
1.54 A° 1.34 A°

C-C Bond length : 1.49 A°

C-C BL: Alkane > Benzene > Alkene > Alkyne (1.20 A°)
(Benzene → Area of resonance)
1.54 A° 1.39 A° 1.34 A°

b) 

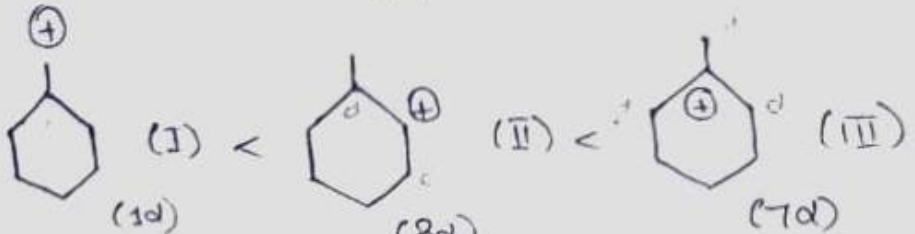
C-C Bond length : 1.39 A°

iii) Stability of carbocation :

$\overset{\oplus}{C}H_3 < CH_3 - \overset{\oplus}{C}H_2 < CH_3 - \overset{\oplus}{C}H - CH_3 < CH_3 - \overset{\oplus}{C}(CH_3)_2 - CH_3$

Stability : (3α) (6α) (9α)

Stability : $\overset{\alpha}{CH_3} - \overset{\oplus}{C}H - \overset{\alpha}{CH_3} > \overset{\alpha}{CH_3} - \overset{\oplus}{C}H - \overset{\alpha}{CH_2} - CH_3$
(2°) (6α) (2°) (5α)



Stability : $CH_3 - \overset{\oplus}{C}(CH_3)_2 > CH_3 - CH_2 - \overset{\oplus}{C}H - CH_2 - CH_3$

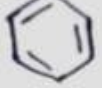
(9α - hydrogen) (6α - hydrogen)

Stability : $CH_2 = CH - \overset{\oplus}{C}H_2$ < $CH_3 - \underset{CH_3}{\overset{|}{\overset{\oplus}{C}}}$ (9d-H)

Allyl carbocation (mesomeric effect)

3° Butyl carbo cation (I|HC)

Stability : $ph - \overset{\oplus}{C}H_2$ < $CH_3 - \underset{CH_3}{\overset{|}{\overset{\oplus}{C}}}$ (More no. of α-hydrogen (α-HC structures)



(mesomeric effect)

(I|HC)

Stability : $ph - \overset{\oplus}{C}H_2 > CH_3 - CH_2 - \underset{CH_2 - CH_3}{\overset{|}{\overset{\oplus}{C}}}$

Here mesomeric effect is dominative (More HC structures)

Stability : $CH_2 - \overset{\oplus}{C}H = CH_2$ (I) (M)

$CH - \overset{\oplus}{C}H \equiv CH_2$ (II) (M|HC)

CH_3 (3d-H)

H_3C (d) $C^+ - CH = CH_2$ (III) (HC|M)

CH_3 (d) (6d-H)

Stability : I < II < III

H_3C (d) CH_3 (d) $C^{\oplus} - CH = CH_2$ (6d) I < H_3C (d) CH_3 (d) $C^{\oplus} - CH = CH - CH_3$ (d) (2d) II

Stability : I < II

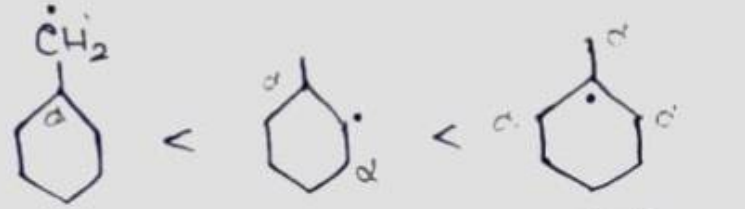
iv) Stability of free radicals :

$\dot{C}H_3 < \overset{\alpha}{C}H_3-\dot{C}H_2 < \overset{\alpha}{C}H_3-\dot{C}H-\overset{\alpha}{C}H_3 < CH_3-\overset{CH_3}{\underset{CH_3}{\dot{C}}}$

(1°) (2°) (3°)

(3α) (6α) (9α)

Stability :



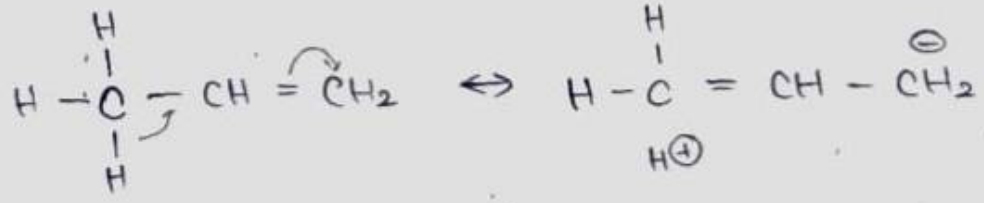
(1°) (2°) (3°)

(1α) (3α) (7α)

* Reverse Hyper conjugation :

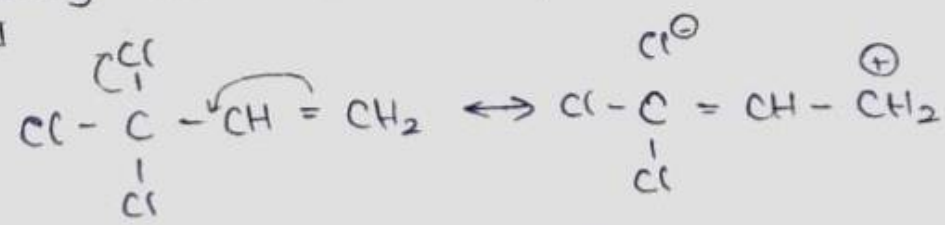
a) $CH_3-CH=CH_2$

+I



b) $CCl_3-CH=CH_2$

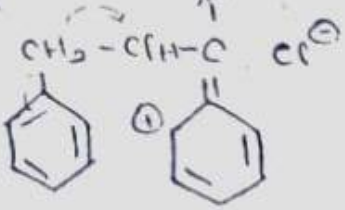
-I



Shifting of π-bonding $e^{\ominus}$ to α_{C-Cl} bonds, ie reverse HC. This is due to electron withdrowing nature of halogens.

$CH_2=CH-\underset{\alpha}{CH_2}Cl$ ✓ (-I)

$CH_2=CH-\underset{\alpha}{CH}Cl_2$ ✓



$CH_2=CH-\underset{\alpha}{CCl_3}$ ✓

$ph-CH_2Cl$ ✓

$ph-CHCl_2$ ✓ $ph-CCl_3$ ✓

(*) Aromaticity :

Aromatic

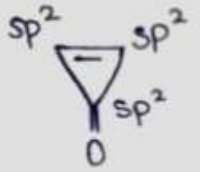
Huckle's rules

* Cyclic
* Planar (sp^2)
* $(4n+2)\pi e^{\ominus}$

$n = 0, 1, 2, 3, \ldots$

$n = 0$; $2\pi e^{\ominus}$

$n = 1$; $6\pi e^{\ominus}$ ....



(Anti-aromatic)

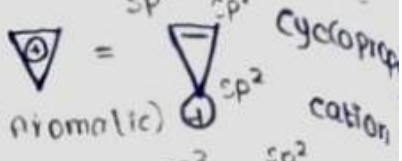
Anti-aromatic

* Cyclic
* Planar (sp^2)
* $4n\pi e^{\ominus}$

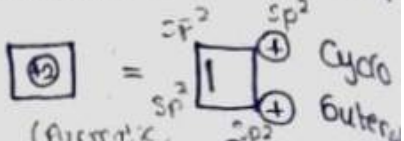
$n = 1, 2, 3, \ldots$

Non-aromatic

* Non-planar

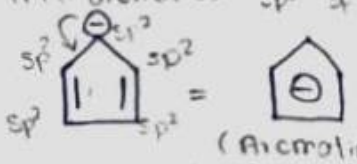


Cyclopropenyl cation

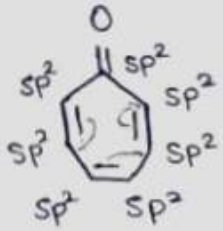


Cyclo butenyl cation

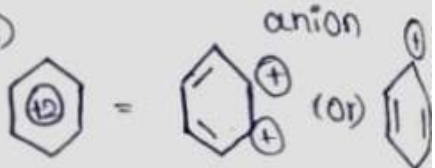
Cyclo penta dienyl cation



Cyclo pentadienyl anion



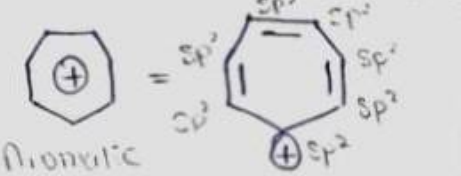
(Tropone) (Aromatic)



Cyclo hexadienyl (Anti-aromatic) cation

(Aromatic) (Tropolone)

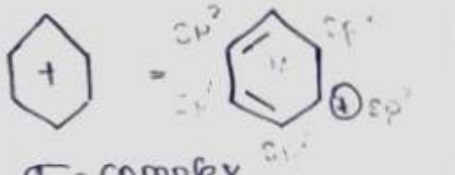
Pyrrole (Aromatic)



Tropelium carbocation

(Aromatic) (Furan)

(Thiophene) (Aromatic)



σ-complex (Non planar)

$CH_3 - CH_2 - \ddot{O} - H$ (sp^3)

$CH_2 = CH - \ddot{O} - H$ (sp^2)

(Pyridine) (Aromatic)

(*) Annulenes :

4-Annulene

(Aromatic)

6-Annulene

(10-Annulene)

Non-aromatic

(Tub-shape)

(Non-planar)

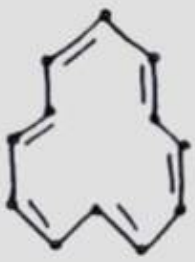
Non-aromatic

8πe⊖

Cyclooctatetraene

(8-Annulene)

(Anti-aromatic)



Cyclic | planar

(12 - 4nπe⊖

Annulene)

(Anti-aromatic)

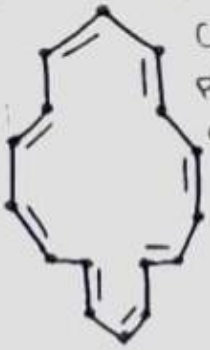
(10πe⊖)

(Aromatic)

Cyclic | planar

(4n+2)πe⊖

(14-Annulene)

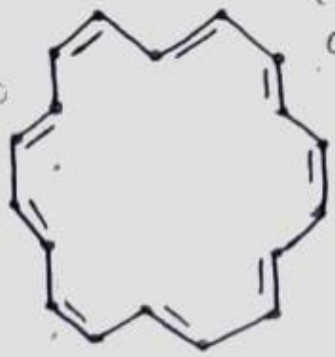


Cyclic

planar

4nπe⊖

(16-Annulene)



(Aromatic)

Cyclic

planar

(4n+2)πe⊖

(18-Annulene)

Eg:

(Non-planar)

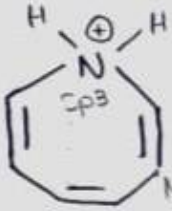
(Non-aromatic)

8πe⊖

Cyclic

planar

(Anti-aromatic)

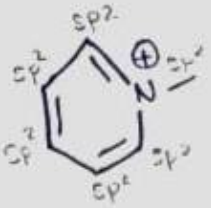


Non-planar

(Non aromatic)

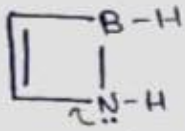
6πe⊖

(Aromatic)

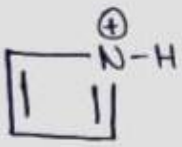


(Aromatic)

4πe⊖ (Anti-aromatic)

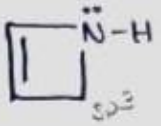


(Anti-aromatic)



4πe⊖

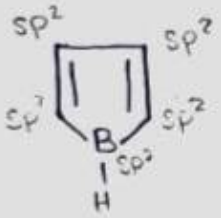
Anti-aromatic



Non-aromatic

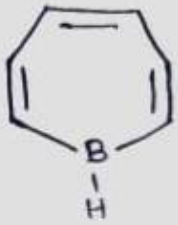
4πe⊖

Anti-aromatic



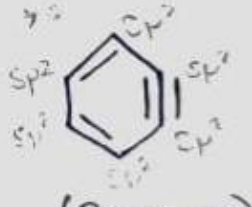
4πe⊖

Anti-aromatic



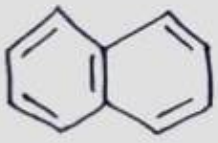
6πe⊖

Aromatic



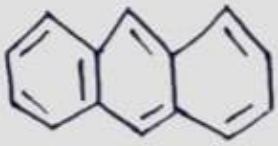
(Benzyne)

(Aromatic)



(Naphthalene)

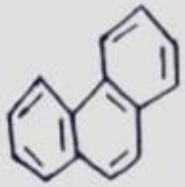
10πe⊖ (Aromatic)



14πe⊖

(Aromatic)

(Anthracene)



14πe⊖

Aromatic

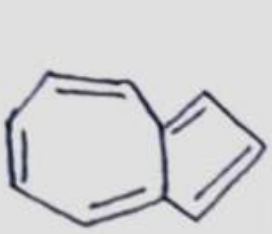
(phenanthrene)

Not included in aromatic

(Pyrene)

Craig's rule)

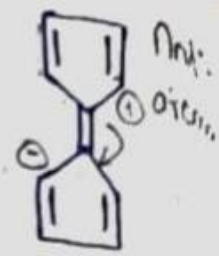
(Pyrene) Aromatic 14πe⊖



(Azulene) (Aromatic)

(Anti-aromatic)

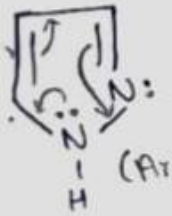
(Aromatic)



(Aromatic)

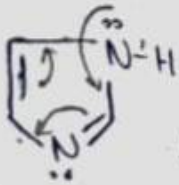
(Aromatic)

Anti-aromatic



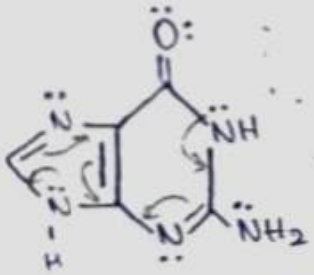
(Aromatic)

(pyrazole)



(Imadazol)

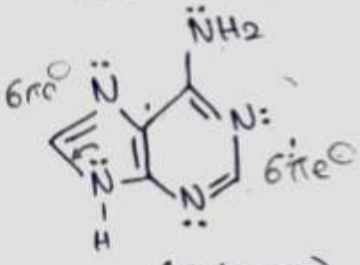
(Aromatic)



(Guanine)

(Aromatic)

Aromatic



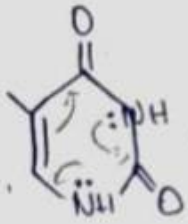
(Adenine)

(Aromatic)

(cytosine)

(Aromatic)

(Uracil)



(Thymine)

(Aromatic)

*) Types of cleavage in a covalent bond:

i) (Homolytic cleavage) ii) (Heterolytic cleavage)

i) In homolytic cleavage equal sharing of $e^{\ominus}$ pairs can take place. It can take place in presence of non-polar solvents.

Eg: $Cl-Cl \rightarrow \dot{Cl} + \dot{Cl}$

Cl_2 (Homolytic) (Free radical)

ii) In heterolytic cleavage unequal sharing of $e^{\ominus}$ pair can take place. It can take place in presence of polar protic solvents.

Eg: $H\overset{\cdot\cdot}{C}l \longrightarrow H^+ + Cl^-$ (Nucleophile)

(Electrophile)

CH_3-CH_3 —Homolysis→ $\dot{C}H_3 + \dot{C}H_3$ (Free radicals)

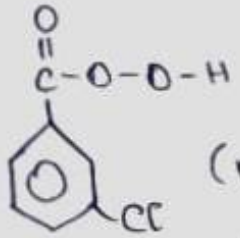
—Heterolysis→ $CH_3^{\oplus}$ + $CH_3^{\ominus}$ (carbanion)

Carbonium ion / Carbo cation)

* Homolysis can take place in presence of HELP (Heat, Electricity, Light, Peroxides)

$-O-O-$ (Peroxides)

H_2O_2 : ; Ph_2O_2 : $Ph-O-O-Ph$



(mCPBA)

(m-chloro per benzoic acid)

*) Attacking reagents / organic reagents :

1) Electrophiles 2) Nucleophiles

1) Electrophiles:

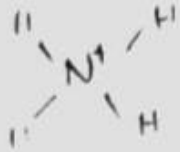
Electron deficient species or electron pair acceptors are electrophiles. Electrophiles are of two types: charged and neutral electrophiles.

* Charged electrophiles : Eg - Positively charged species

H^+, Br^+, CCO^+, NO^+, NO_2^+, SO_3H^+, SO_2H^+, R^+, Cl^+ ...

Except cations of IA, IIA and NH_4^+ ↓ Carbo cation

Li^+, Na^+, K^+, Rb^+, Cs^+, Be^{+2}, Mg^{+2}, Ca^{+2},

Sr^{+2}, Ba^{+2}, NH_4^+. 

* Neutral electrophiles:

Eg: i) Electron deficient species.

BeH_2, BCl_3, BBr_3, BI_3, $BeCl_2$, $BeBr_2$, B_2H_6,

$SnCl_2$, ...

ii) Central atom having octet electronic configuration with availability of vacant orbitals.

PCl_3, $AsCl_3$, $SnCl_4$, NCl_3 (X), CCl_4 (X)

iii) Central atom having more than octet with availability of vacant orbitals.

PCl_5, SF_6, IF_7

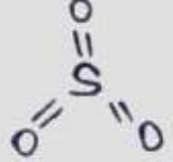
iv) Neutral species like free radicals, carbenes and nitrenes. R°; CH_3°, $CH_3\dot{C}H_2$, $CH_3-\dot{C}H-CH_3$

$:CH_2$ → Carbenes, $:CCl_2$, $:CBr_2$, $:CI_2$, $:CF_2$

Nitrenes: $H-\ddot{N}:$, $R-\ddot{N}:$ (Alkyl nitrene), $R-\overset{O}{\overset{\|}{C}}-\ddot{N}:$ (Acetyl nitrene (OR) Acyl nitrene)

v) Neutral species having multiple bonds in between different atoms.

CO_2 : $O=C=O$; CS_2 : $S=C=S$; SO_2 : ;

SO_3 : 

vi) CC_2, Br_2, I_2 (Halogens) are also examples of neutral electrophiles.

vii) D-block elements like $FeCl_3$, $ZnCl_2$, ... also act as electrophiles due to vacant d-orbital.

2) Nucleophiles:

Electron rich species or electron pair donors are nucleophiles.

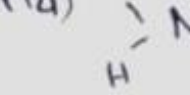
* Charged nucleophiles:

Negatively charged species (Cl^-, Br^-, I^-, NO_2^-, NO_3^-, HSO_4^-, SO_4^{-2}, CO_3^{-2}, F^-, ...)

* Neutral nucleophiles:

i) Central atom having atleast one lone pair of electron can act as neutral nucleophiles.

i) $\ddot{N}H_3$, $R-\ddot{N}H_2$ (1°), $R_2\ddot{N}H$ (2°), $R_3\ddot{N}$ (3°), $\ddot{N}H_2-\overset{\overset{O}{\|}}{C}-\ddot{N}H_2$,

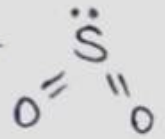
a) $\ddot{N}H_2-OH$ (Hydroxyl amine), (N_2H_4)  , ...

b) $H_2\ddot{O}$:, $R-\ddot{O}-H$ (Alcohol), $R-\ddot{O}-R$ (Ether)

c) $H_2\ddot{S}$:, $R-\ddot{S}-H$ (Thioalcohol), $R-\ddot{S}-R$ (Thioether)

d) $\ddot{P}H_3$, $Ph_3\ddot{P}$, $Ph_2\ddot{P}H$, $Ph\ddot{P}H_2$

(Phosphine) (Triphenyl phosphine) (Diphenyl phosphine) (Phenyl phosphine)

*  can act as both electrophile and nucleophile.

ii) Central atom having multiple bonds with similar atoms.

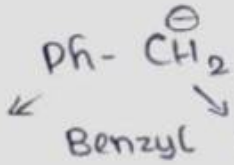
Alkenes : C_2H_4 ($H_2C=CH_2$)

Alkynes : C_2H_2 ($HC\equiv CH$) ; Alkadienes : $CH_2=CH-CH-CH=CH_2$

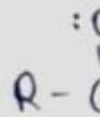
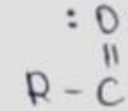
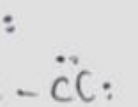
Benzene :

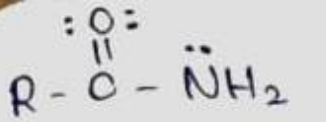
Ambidentate nucleophiles :

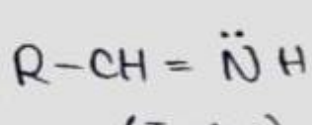
Species having two nucleophilic centres, among them, one is neutral & other one is charged are called ambidentate nucleophi



Benzyl carbanion

Note : Organic compounds behaves as both electrophiles and nucleophiles are ,  , ,  , , ,  ,



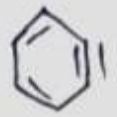
, 

(Imine)

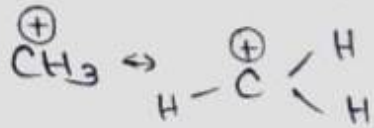
Reactive Intermediates :

* Carbocation (R^+) ; * Carbanion (R^-) ;

* Free radicals ($\dot{R}$) ; * Carbenes ($:CH_2$) :

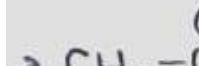
* Nitrenes ($H-\ddot{N}:$) ; * Benzyne 

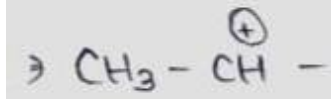
*) Carbocation :

Eg : 

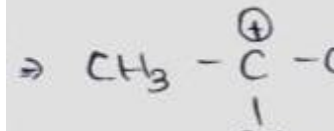
(sp^2, trigonal planar)

↘ Diamagnetic

⇒  (1°) | Ethyl carbo cation

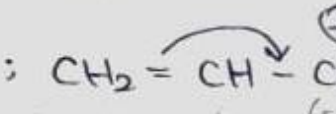
⇒  | $(CH_3)_2\overset{\oplus}{C}H$ (Isopropyl carbocation)

(2°)

⇒  | $(CH_3)_3\overset{\oplus}{C}$ (3° butyl carbocation)

(3°)

⇒ (sp) ; ⇒ (not aromatic) (phenyl carbocation) :

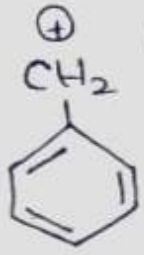
Vinyl carbocation : 

⇒

(Allyl carbocation)

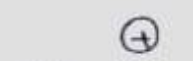
(Benzyl carbocation)

⇒ (1°) :



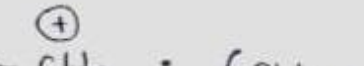
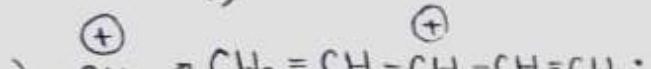
(-M)

(+M)

; 

(-I)

$Ph_2\overset{\oplus}{C}H$ (2°) ; $Ph_3\overset{\oplus}{C}$ (3°)

⇒ ;  →  ;

(1°) (2°) $(CH_2=CH)_3C^{\oplus}$ (3°)

Stability of carbocation : $\alpha + I$

(T | M | HC) $\alpha : M$

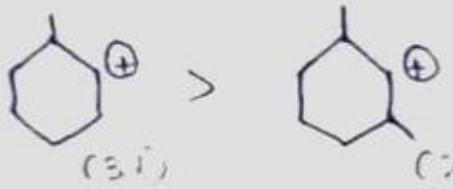
α HC

*) $CH_3^{\oplus}$ < $CH_3-CH_2^{\oplus}$ < $CH_3-\overset{\oplus}{C}H-CH_3$ < $CH_3-\overset{CH_3}{\underset{|}{C}}-\overset{\oplus}{C}H_3$

(1°) (2°) (3°)

*) $CH_3-\overset{\oplus}{C}H_2$ > $CH_2=\overset{\oplus}{C}H$ > $CH\equiv\overset{\oplus}{C}$

sp^2 sp

*) > 

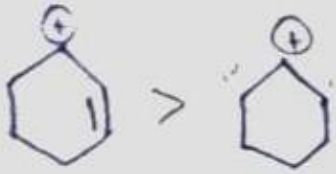
(3°) (2°)

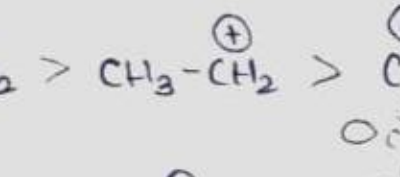
*) $CH_3-\ddot{O}-\overset{\oplus}{C}H_2$ > $CH_3-CH_2-\overset{\oplus}{C}H_2$

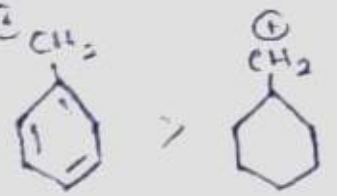
(lone pair conjugation resonance)

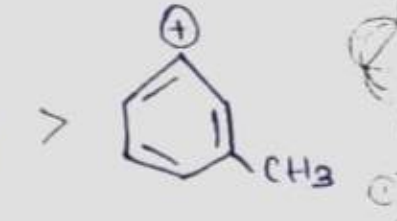
*) >

*)

*) 

*) 

*) 

*) 

*) $ph-\overset{\oplus}{C}H_2$ $ph_2\overset{\oplus}{C}H$ $ph_3\overset{\oplus}{C}$

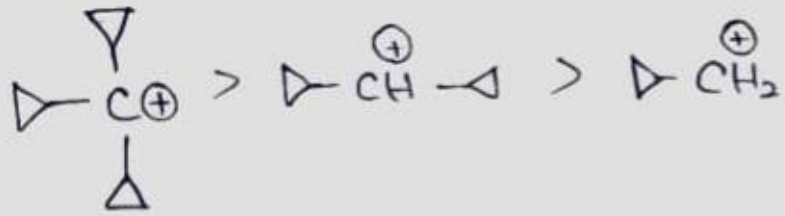
*) $CH_2=CH-\overset{\oplus}{C}H_2$ $(CH_2=CH)_2\overset{\oplus}{C}H$ < $(CH_2=CH)_3\overset{\oplus}{C}$

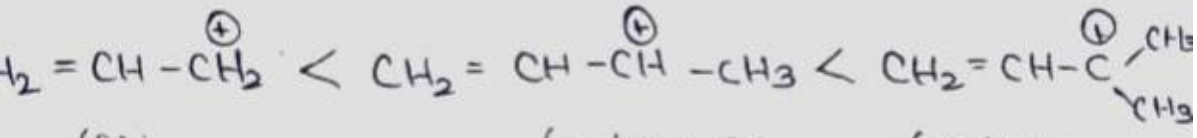
*) $ph-\overset{\oplus}{C}H_2$ < $CH_2=CH-\overset{\oplus}{C}H_2$

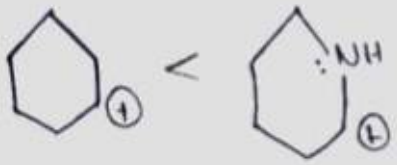
*) $ph-\overset{\oplus}{C}H_2$

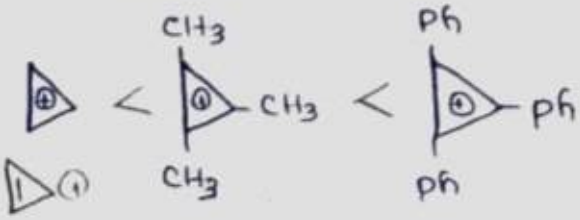
*) $ph-\overset{\oplus}{C}H_2$ $CH_3-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-\overset{\oplus}{C}H_2$

*) $CH_2=CH-\overset{\oplus}{C}H_2$

*) 

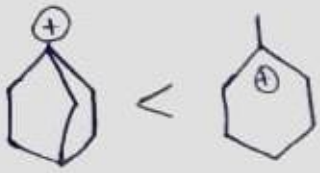
*) 
(1°) (1°/2°) 2d (1°/3°) 6d

*)  *)

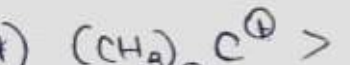
*) *) 

*)
(3°) (2d) (6d) (2d)

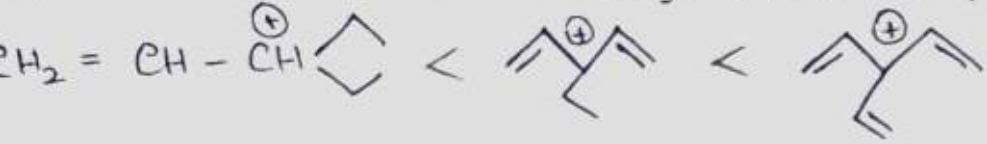
*)
(3°) (3°) (2°) (1°)

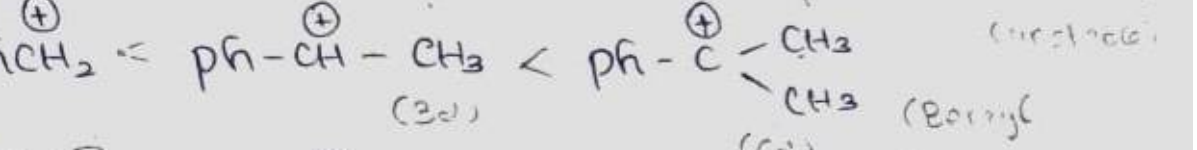
*) 

*)
(2d) H is donating factor

*) 

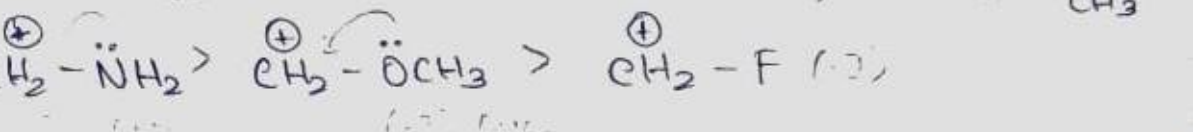
According to Bredth's rule, positive charge should not be present on the bridge carbon, otherwise

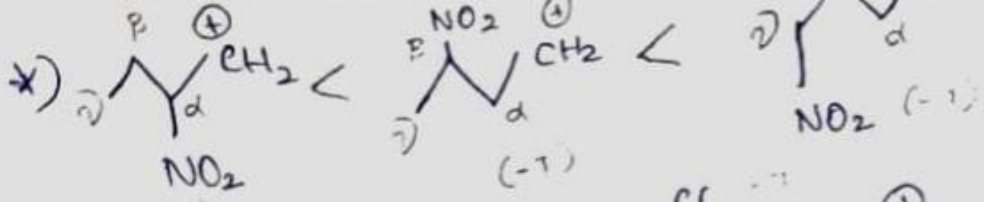
*) 

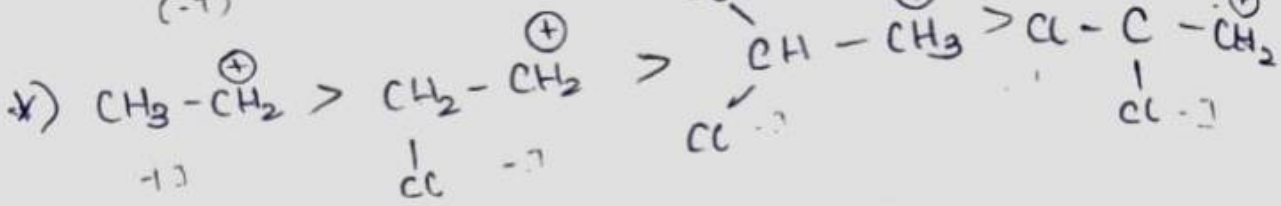
*) 
(3d) (6d) (Benzyl carbocation)

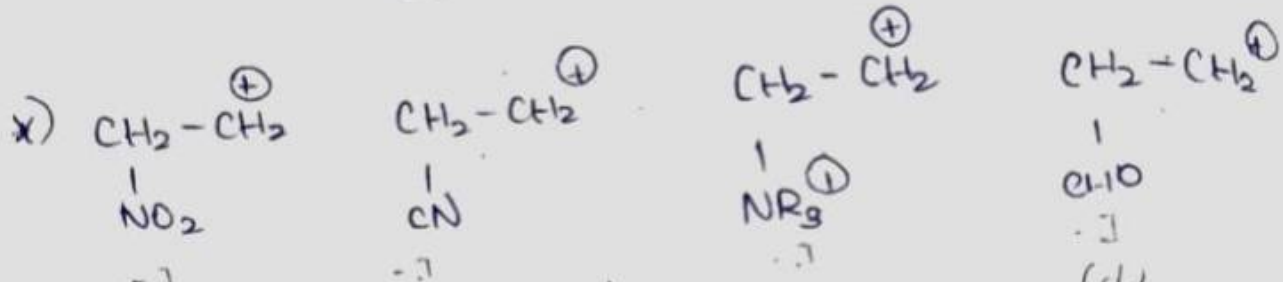
*)

*)
(2°) (3°)

*) 

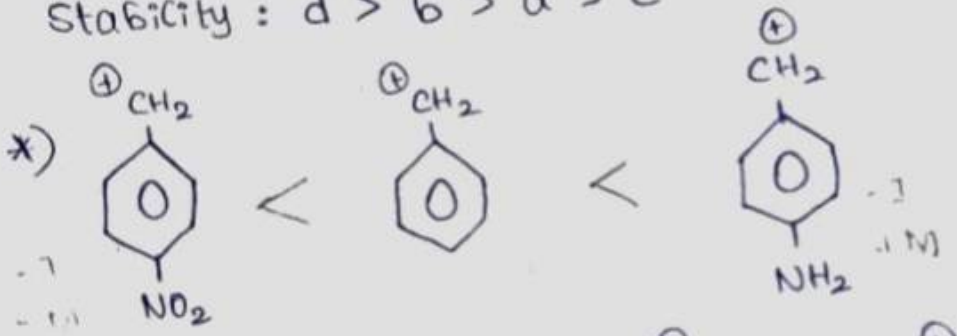
*) 

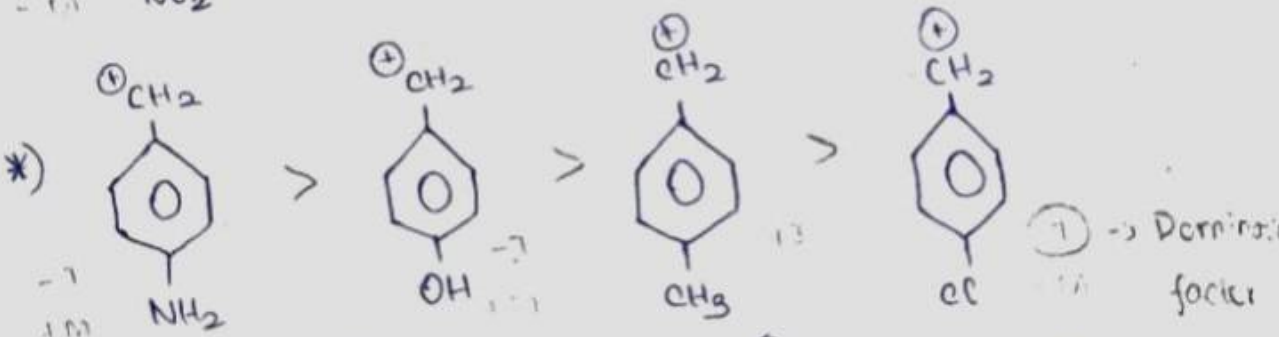
*) 

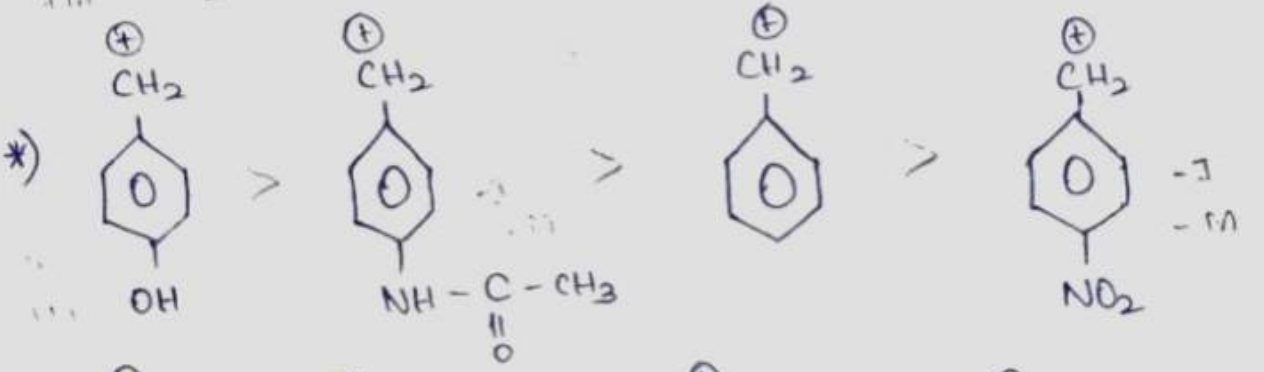
*) 

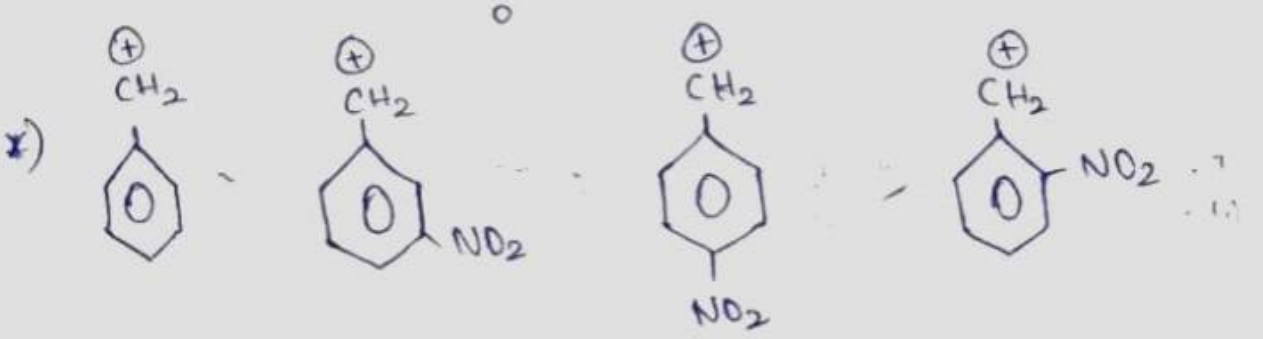
(a) (b) (c) (d)

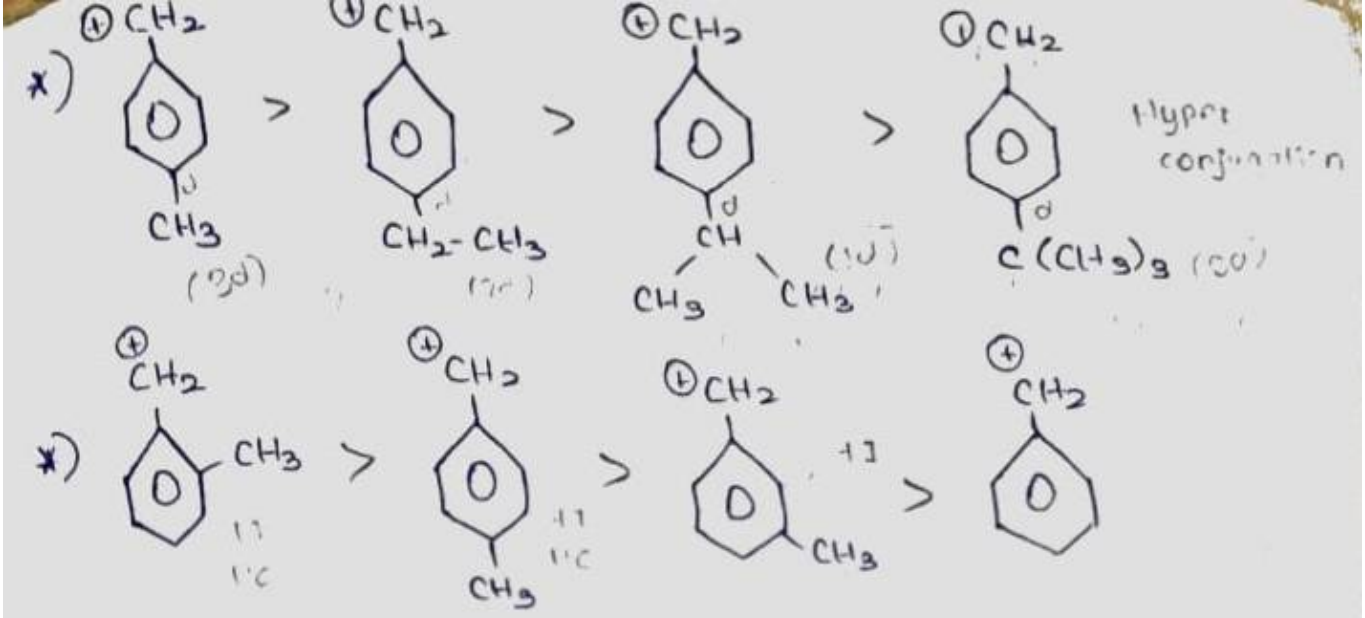
Stability : d > b > a > c

*) 

*) 

*) 

*) 

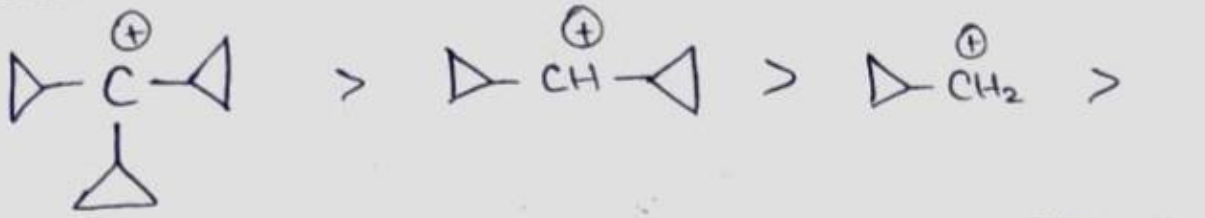


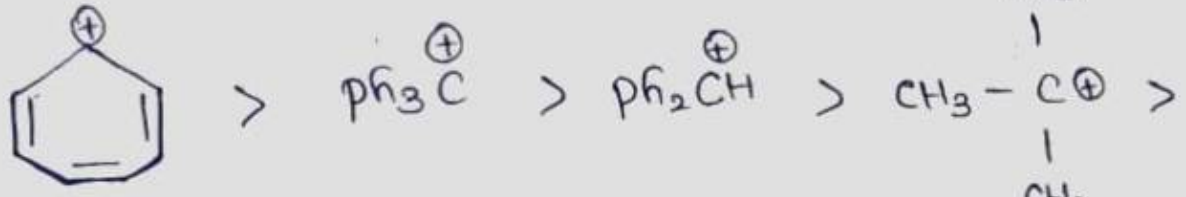
[*) Hyperconjugation is possible only in ortho and para positions.]

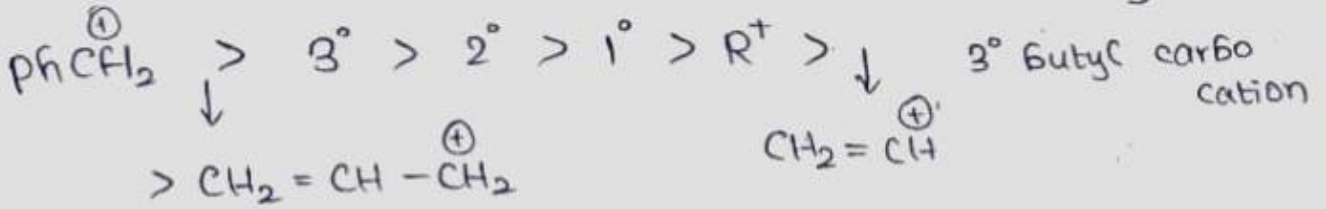
+I, +M → Electron Releasing groups

-I, -M → Electron Withdrawing groups

*) Overall stability of carbocation :



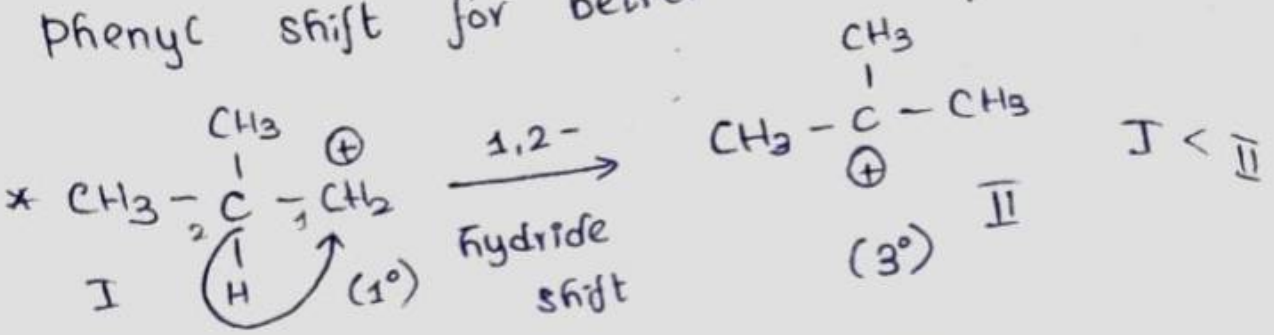


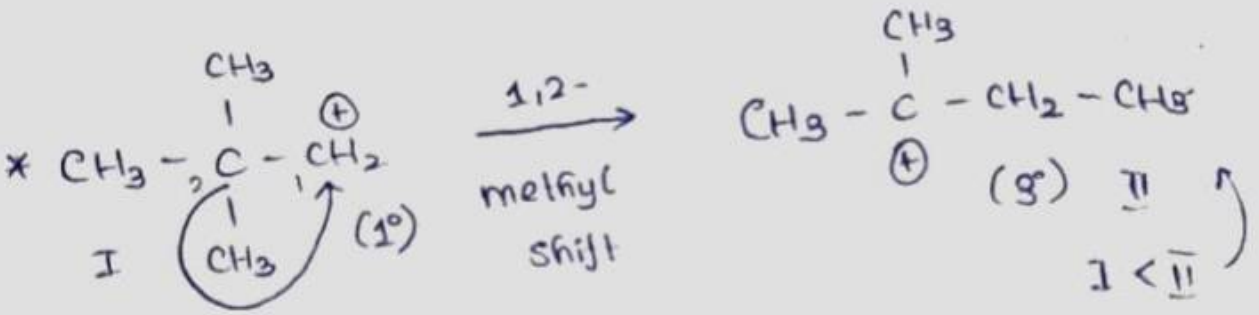


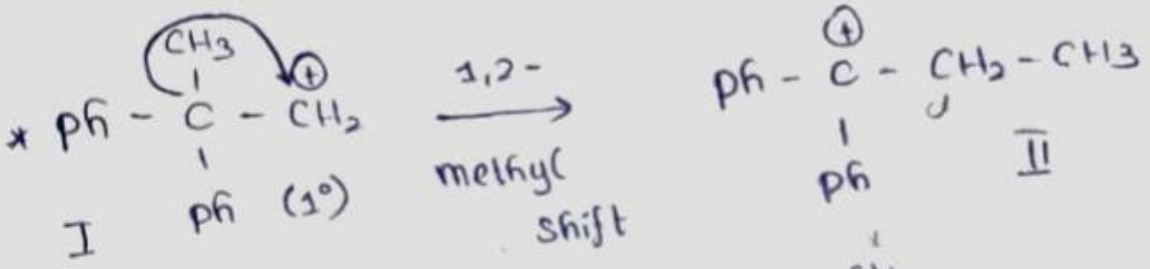
* Special properties of carbocation :

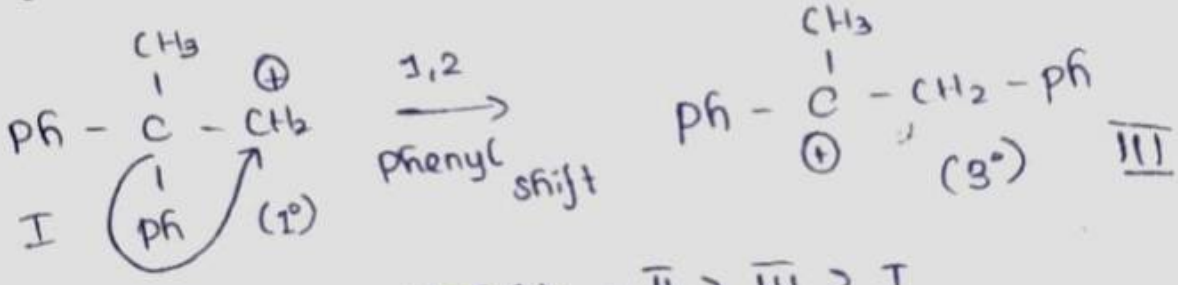
i) Carbocation undergoes rearrangement by 1,2-hydride shift : 1,2-methyl shift, 1,2-

Phenyl shift for better Stab.

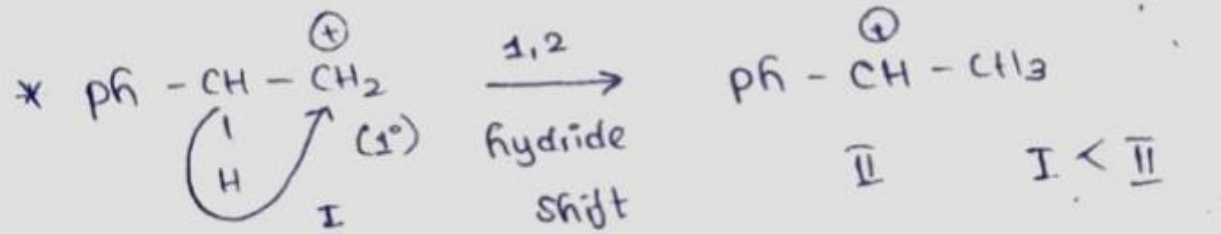


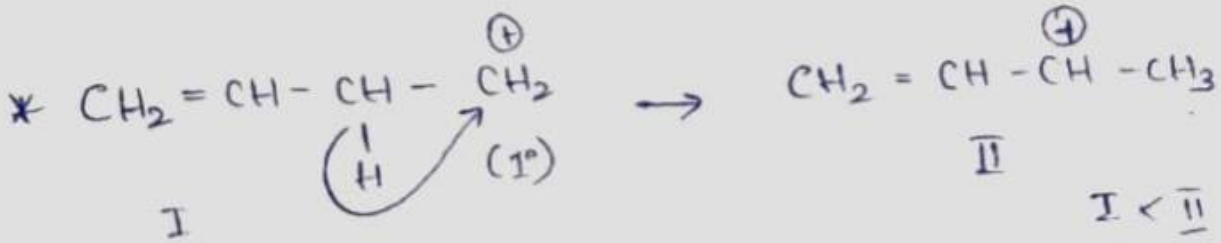


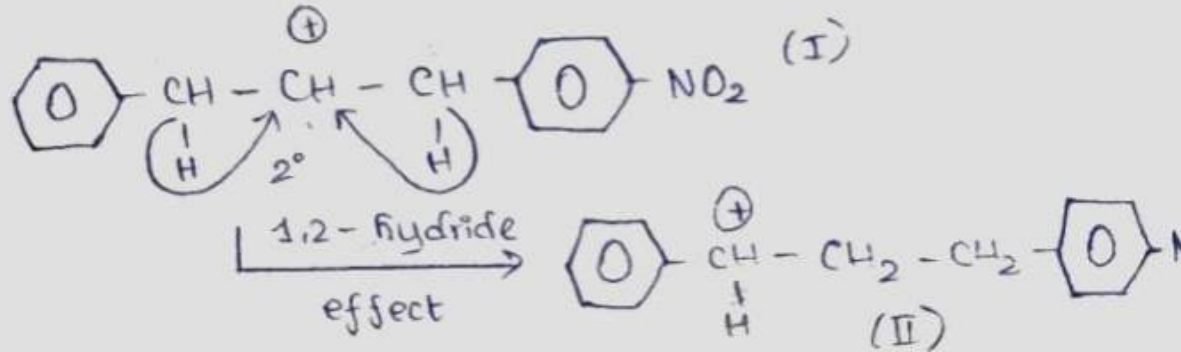


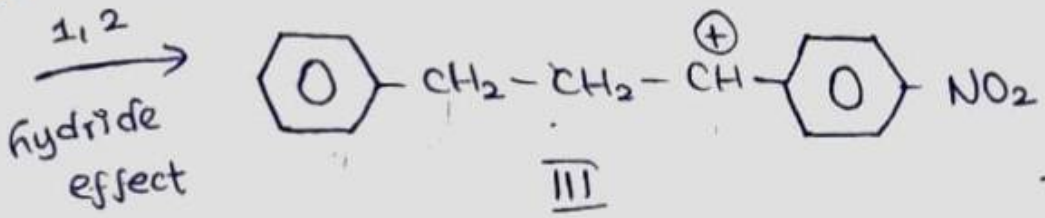


Stability : II > III > I

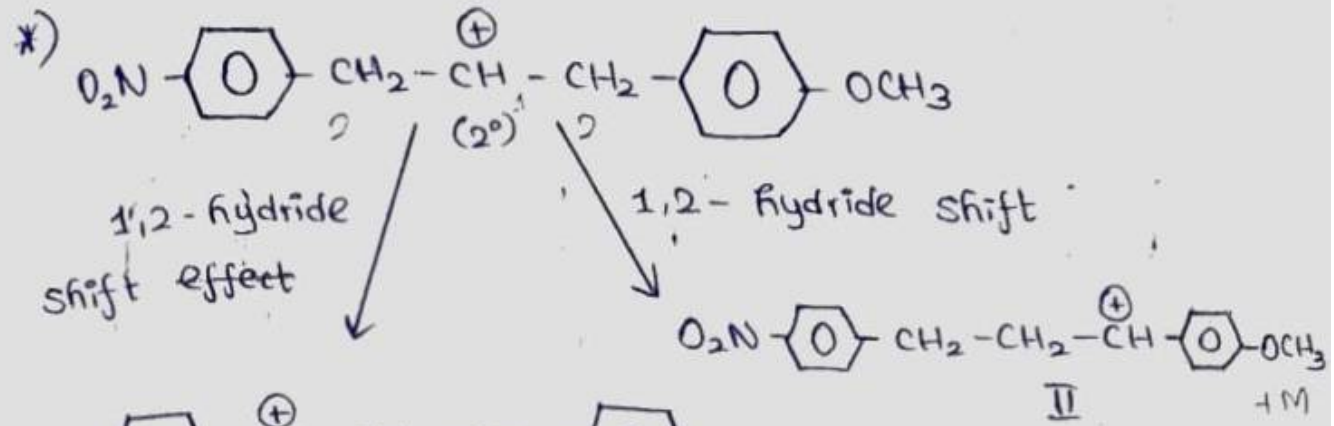








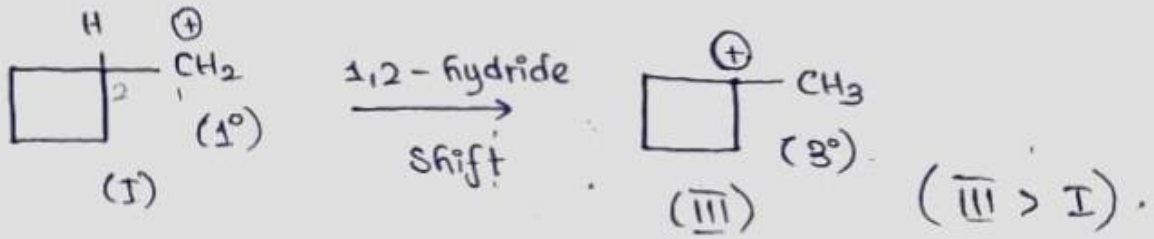
Stability : II > III > I

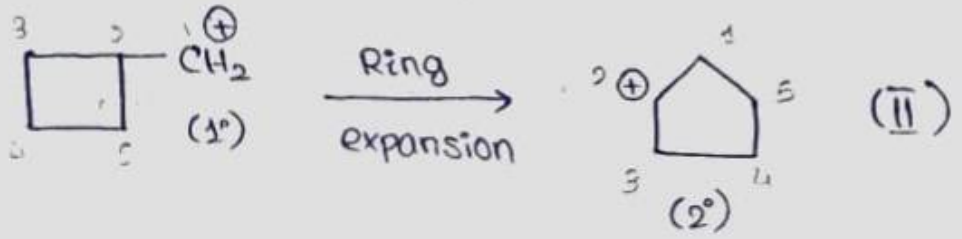


Stability : II > I

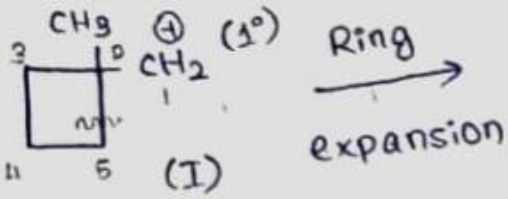
2) Carbocation undergoes ring expansion for better stability.

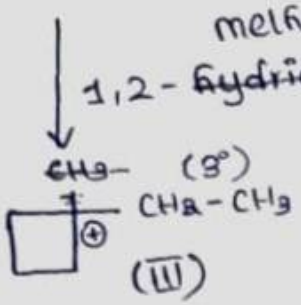
*) Stability : hexagon > pentagon > square > triangle



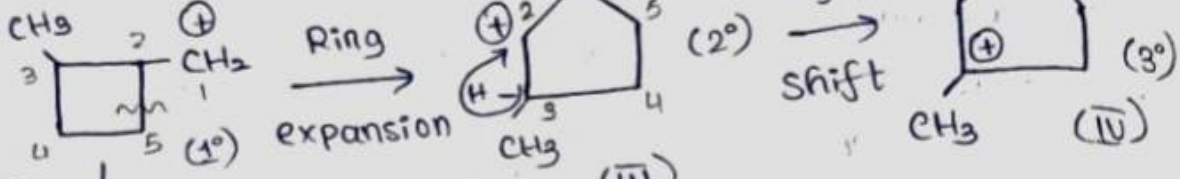


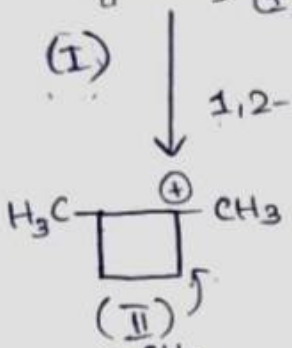
Stability : II > III > I

*) 

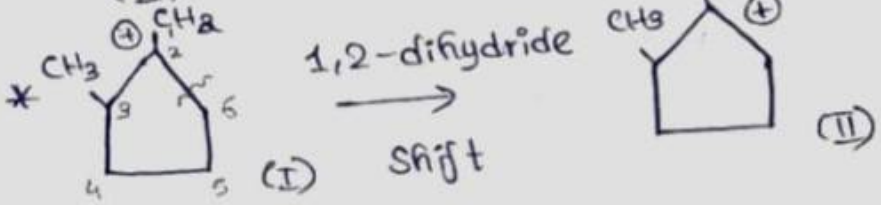


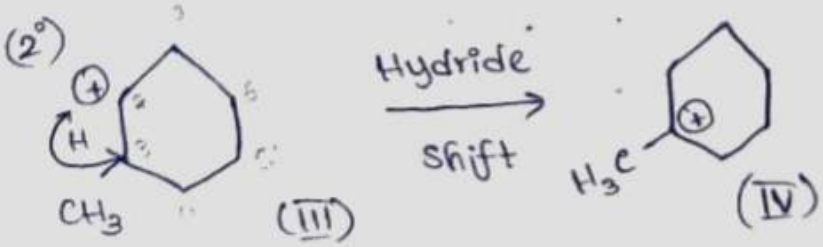
Stability : II > III > I

*) 



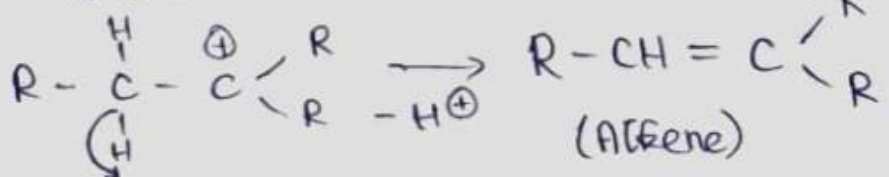
Stability : IV > III > II > I



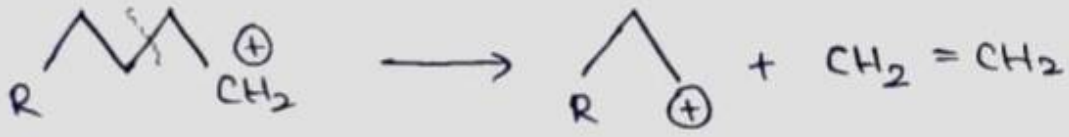


Stability : IV > III > II > I

3) In some rxns carbocation can act as bronsted acid.



4) In some reactions carbocation undergoes fragmentation.



5) In some reactions carbocation undergoes intramolecular alkylation.

6) $R^+ + Nu^{\ominus} \rightarrow R-Nu$

(Nucleophile)

Electrophile

*) Generation of carbocation : (R^+)

1) Heterolysis of alkyl halide (R-X)

$$R-X \rightarrow R^{\oplus} + X^{\ominus}$$

2) Heterolysis of oxonium ion :

(Nucleophile) (Electrophile) Oxonium ion

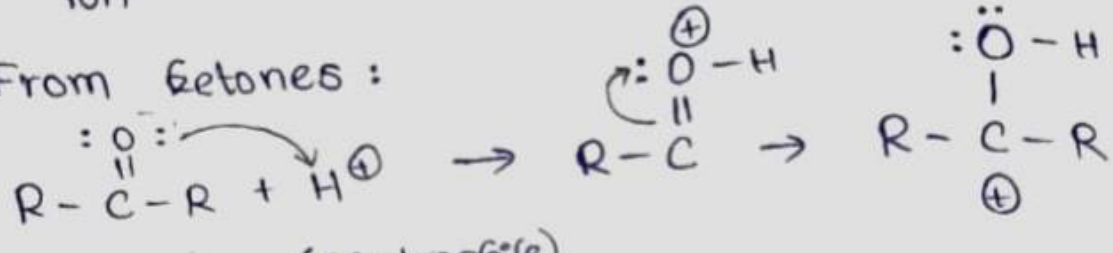
(Lewis base) (Lewis acid)

Ether (Lewis base) (Lewis acid) oxonium ion

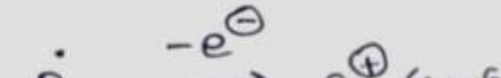
3) Heterolysis of alkyl diazonium ion :

Alkyl diazonium ion

4) From ketones :



(Nucleophile) (Electrophile)

5) 

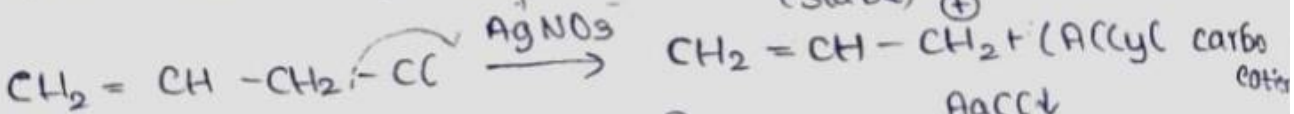
(Free radical)

$\downarrow + e^{\ominus}$

R^-

(Carbanion)

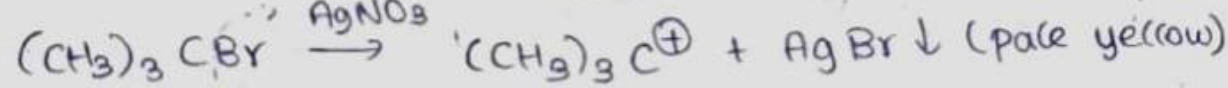
Q) Which of the following forms AgCl ↓ (white PPT) on rxn with $AgNO_3$.



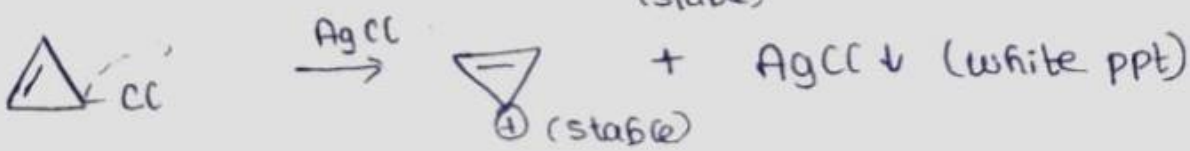
(stable) (Allyl carbocation)

AgCl↓

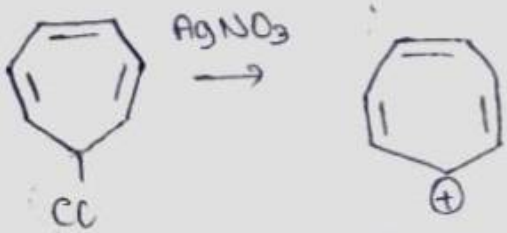
stable



(stable)



(stable)



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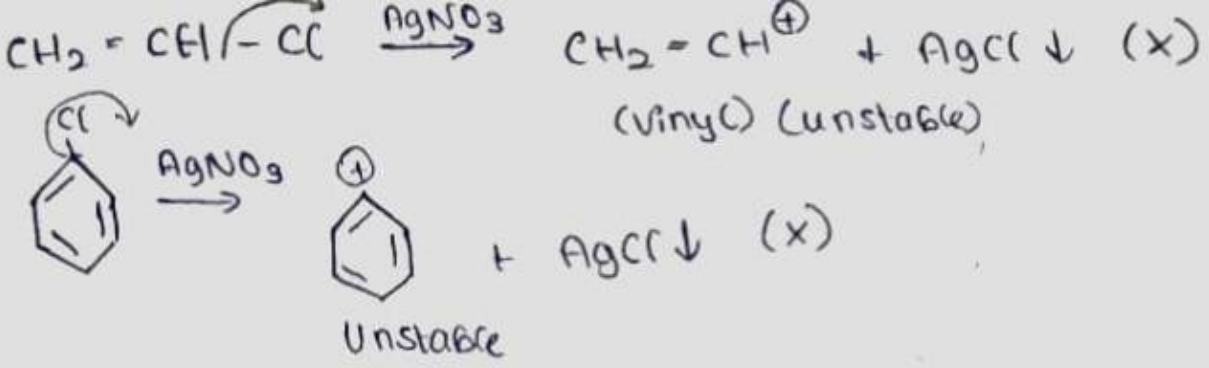
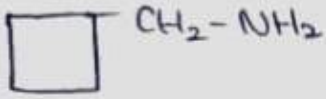


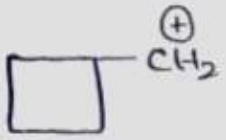
$R^+ + Nu^- \rightarrow R-Nu$

* $R-CH_2-NH_2$ (1° Amine) $\xrightarrow[(OR)\ HNO_2]{NaNO_2 + HCl}$ $R-CH_2OH$

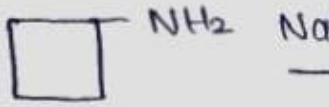
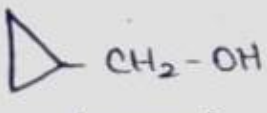
$R-\overset{\oplus}{C}H_2$ (carbocation)

*  $\xrightarrow[HNO_2]{NaNO_2 + HCl}$ (Major)

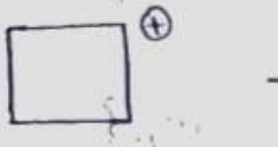
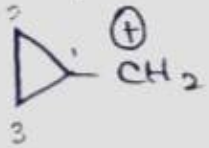
Cyclo Butyl methyl amine

 $\xrightarrow{\text{Ring expansion}}$

OH^-

*  $\xrightarrow[HNO_2]{NaNO_2 + HCl}$ 

Cyclo Butyl amine (major)

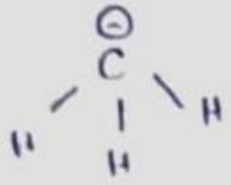
 $\xrightarrow{\text{Ring contraction}}$ 

OH^-

*) Cyclo alkyl methyl amine undergoes ring

expansion whereas cyclo alkyl undergo ring contraction.

(2) Carbanion :

*) $CH_3^{\ominus}$  sp^3, 1LP, Pyramidal

Diamagnetic

$CH_3 - CH_2^{\ominus}$; $CH_3 - CH^{\ominus} - CH_3$ | $(CH_3)_2 CH^{\ominus}$

Ethyl carbanion (1°) ; (Isopropyl carbanion)

$CH_3 - \underset{\underset{CH_3}{|}}{C^{\ominus}} - CH_3$: $CH_2 = CH^{\ominus}$ (sp^2)

Vinyl carbanion

$(CH_3)_3C^{\ominus}$: $CH_2 = CH - CH_2^{\ominus}$ (sp^2)

3° butyl carbanion

Allyl carbanion

(phenyl carbanion) (sp^2) : (sp^2) $C_6H_5 - CH_2^{\ominus}$ | ph- $CH_2^{\ominus}$

Benzyl carbanion

*) Stability of carbanion : (I|M)

It is explained by inductive & mesomeric effect.

α-I ; α-M ; $\alpha \frac{1}{+I}$: $\alpha \frac{1}{+M}$

*) $CH_3^{\ominus}$ < $CH_3 - CH_2^{\ominus}$ < $CH_3 - CH^{\ominus} - CH_3$ < $CH_3 - \underset{\underset{CH_3}{|}}{C^{\ominus}} - CH_3$

*) $CH_3 - CH_2^{\ominus}$ $CH_2 - CH^{\ominus}$ $HC \equiv C^{\ominus}$: (electron withdrawing)

*) $CH_2-\overset{\ominus}{C}H_2$ > $CH_2-\overset{\ominus}{C}H_2$ > $CH_2-\overset{\ominus}{C}H_2$

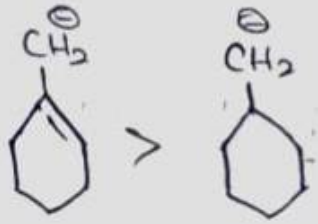
($-CH_2-CH_2-NO_2$; $-CH_2-CH_2-Cl$; $-CH_2-CH_2-OH$)

*) $CH_3-CH_2-\overset{\ominus}{C}H_2$ < $CH_2=CH-\overset{\ominus}{C}H_2$ (+M)

*) $CH_2=CH-CH_2-\overset{\ominus}{C}H_2$ < $CH_2=CH-\overset{\ominus}{C}H_2$

*) $CH_2=CH-\overset{\ominus}{C}H_2$ < $ph-\overset{\ominus}{C}H_2$ (More conjugation)

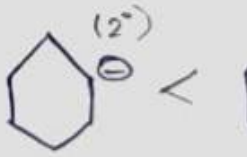
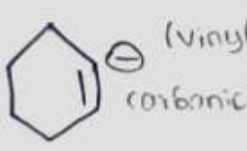
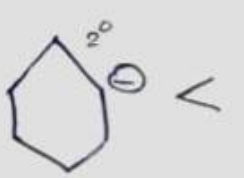
*) $CH_2=CH-\overset{\ominus}{C}H_2$ > $CH_3-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}\ominus$

*) $ph-\overset{\ominus}{C}H_2$ > $CH_3-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}\ominus$; *)  >

Strong $e^{\ominus}$ withdrawing nature

*) $CH_3-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{C}H_2$ > $ph\overset{\ominus}{C}H_2$ > $CH_2=CH-\overset{\ominus}{C}H_2$ > $CH_3-\overset{\ominus}{C}H_2$

(-M)(-I) (Benzyl) (Allyl) (1°)

*)  (2°) <  (vinyl carbonion) ; *)  2° <

In case of carbonation, 2° is more stable

*) $CH_3\overset{\ominus}{C}H_2$ < $CH_2-\overset{\ominus}{C}H_2$ < $O_2N-CH-\overset{\ominus}{C}H_2$ < $(NO_2)_2-\overset{NO_2}{\overset{|}{C}}-\overset{\ominus}{C}H_2$

(+I) (-I) (-I) (-I)

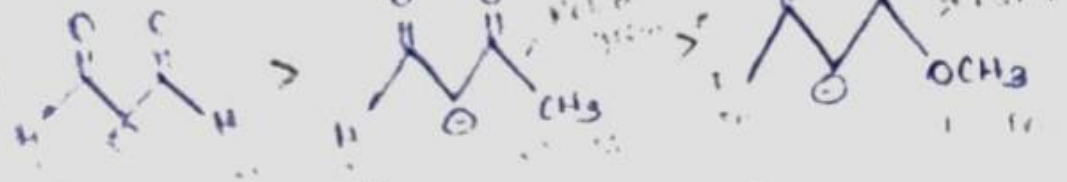
*) $CH_2-\overset{\ominus}{C}H_2$ > $CH_2-\overset{\ominus}{C}H_2$ > $CH_2-\overset{\ominus}{C}H_2$ > $CH_2-\overset{\ominus}{C}H_2$

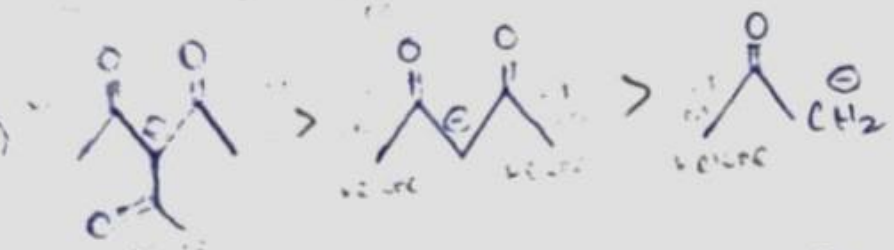
($-CH_2-CH_2-F$; $-CH_2-CH_2-Cl$; $-CH_2-CH_2-Br$; $-CH_2-CH_2-Cl$)

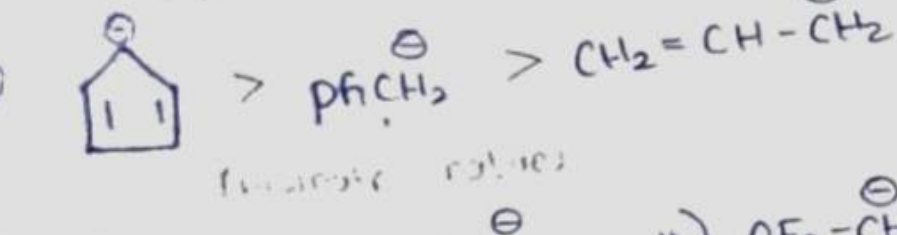
*) $\overset{\ominus}{C}H_2-NO_2$ > $\overset{\ominus}{C}H_2-CN$ > $\overset{\ominus}{C}H_2-CHO$

*) $PhCH_2^{\ominus}$ < $Ph_2CH^{\ominus}$ < $Ph_3C^{\ominus}$

*) ; *)

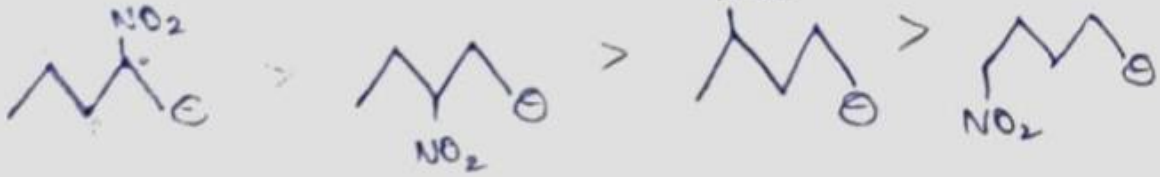
*) 

*) 

*) 

*) > $PhCH_2^{\ominus}$ > $CH_2=CH-CH_2^{\ominus}$ > $CH_2=CH^{\ominus}$

*) $C(NO_2)_3^{\ominus}$ > $Ph_3C^{\ominus}$; *) $CF_3-CH_2^{\ominus}$ > $CCl_3-CH_2^{\ominus}$

*) 

*) $CF_3^{\ominus}$ $CCl_3^{\ominus}$; *) $CH_3-CH^{\ominus}-S-CH_3$ >

*) $CH_3-CH^{\ominus}-P(CH_3)(CH_3)$ $CH_3-CH^{\ominus}(CH_3)(CH_3)$; $CH_3-CH^{\ominus}-CH_3$

*) $CH_2^{\ominus}-N(CH_3)(CH_3)$ $CH_2^{\ominus}-P(CH_3)(CH_3)$

*)

*)

1) Overall stability:

Aromatic > $ph\overset{\ominus}{C}H_2$ (Benzyl) > $CH_2=CH-\overset{\ominus}{C}H_2$ (Allyl) > $HC\equiv\overset{\ominus}{C}$ > ~~Alkyl~~ sp

$CH_2=\overset{\ominus}{C}H$ > $CH_3-\overset{\ominus}{C}H_2$ > $CH_3-\overset{\ominus}{C}H-CH_3$ > $CH_3-\overset{\ominus}{C}(CH_3)_2$

(vinyl) (1°) (2°) (3°)

2) Generation of carbanion ($R^{\ominus}$):

i) From organometallic compounds

(Alkyl → RLi ⟶ $R^{\ominus} + Li^{\oplus}$

Lithium) $CH_3Li \leftrightarrow H_3C-Li \longrightarrow \overset{\ominus}{C}H_3 + \overset{\oplus}{Li}$

$RMgX \longrightarrow R^{\ominus} + MgX^{\oplus}$

(Grignard reagent) $(Mg^{+2} + X^{-})$

$CH_3MgCl \rightarrow \overset{\ominus}{C}H_3 + \overset{\oplus}{Mg}Cl$

2) From carbonyl compounds:

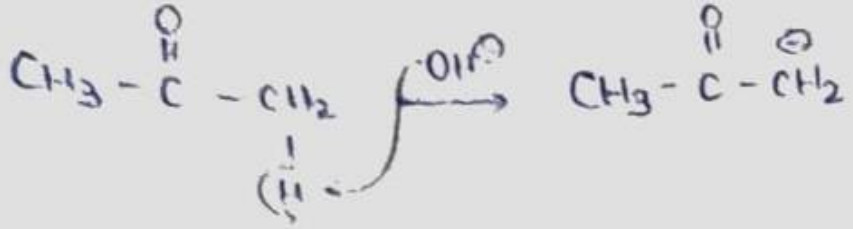
$CH_3-\overset{O}{\overset{\|}{C}}-H \xrightarrow{OH^{\ominus}} \overset{\ominus}{C}H_2-\overset{O}{\overset{\|}{C}}-H$

(3d-H)

$CH_2(H)-\overset{O}{\overset{\|}{C}}-H \xrightarrow{OH^{\ominus}} \overset{\ominus}{C}H_2-\overset{O}{\overset{\|}{C}}-H$ (-I, -M)

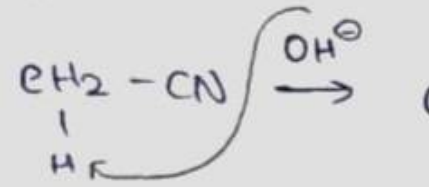
$CH_3-\underset{\alpha}{\overset{O}{\overset{\|}{C}}}-\underset{\alpha}{CH_3} \xrightarrow{OH^{\ominus}} CH_3-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{C}H_2$

-I | -M



3) From alkyl cyanides (RCN) and nitro alkanes ($R-NO_2$) :

Eg: $\underset{\alpha}{CH_3-CN} \xrightarrow{OH^-} \overset{\ominus}{CH_2}-CN$ (-I-M)



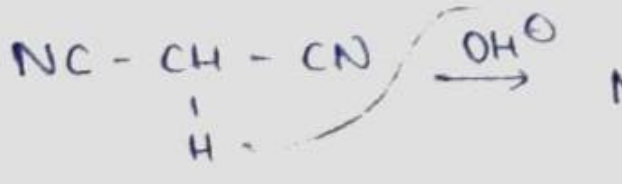
$\underset{\alpha}{CH_3-NO_2} \xrightarrow{OH^-} \overset{\ominus}{CH_2}-NO_2$ (-I-M)

$\underset{\beta}{CH_3}-\underset{\alpha}{CH_2}-NO_2 \xrightarrow{OH^-} CH_3-\overset{\ominus}{CH}-NO_2$

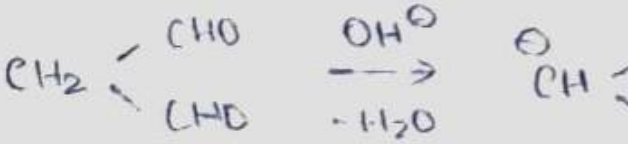
4) From compounds having active methylene group :

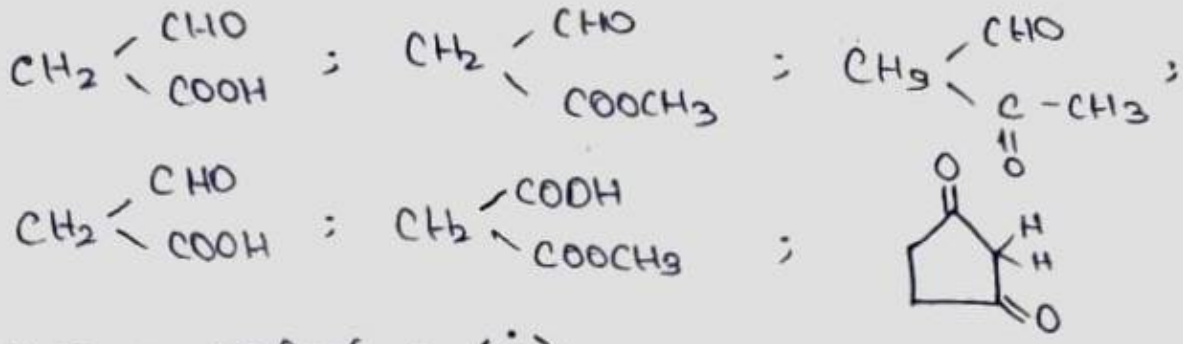
GF : $\underset{\substack{-I\\-M}}{EWG}-CH_2-\underset{\substack{-I\\-M}}{EWG}$

$NC-CH_2-CN \xrightarrow{OH^\ominus} \underset{-I-M}{NC-\overset{\ominus}{CH}-CN}$ (-I-M)



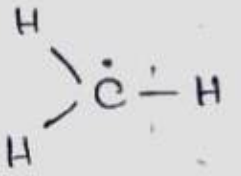
$O_2N-CH_2-NO_2 \xrightarrow[-H_2O]{OH^\ominus} O_2N-\overset{\ominus}{CH}-NO_2$





*) Free radical : ($\dot{R}$)

Eg: $\dot{C}H_3$ (Methyl free radical)



(sp^2, trigonal planar)

* $\dot{C}F_3$ (Trifluoro methyl free radical)

(sp^3, pyramidal)

* $CH_3-\dot{C}H_2$

Ethyl free radical (1°)

* $CH_3-\dot{C}H-CH_3$

Isopropyl free radical (2°)

* $CH_2=\dot{C}H$

(Vinyl)

* $CH_3-\dot{C}(CH_3)_2$ (3° Butyl free radical)

* $CH_2=CH-\dot{C}H_2$

(Allyl free radical)

(They are electrophiles)

Phenyl free radical

Benzyl free radical

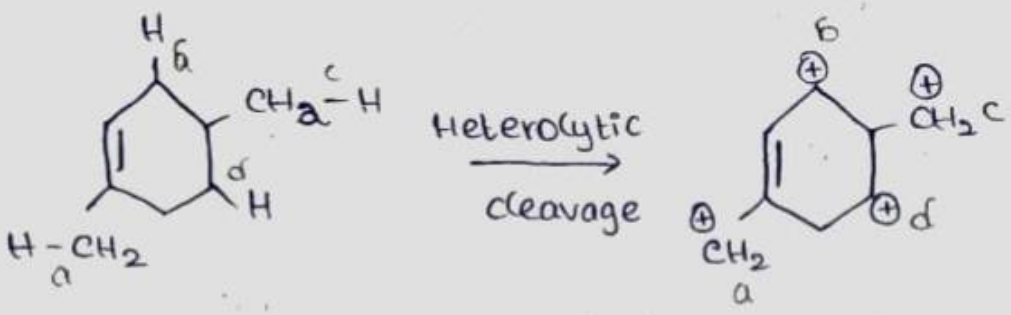
Free radicals are odd electronic species and they are paramagnetic in nature.

Free radicals are electrophiles, which are

formed by homolytic cleavage.

$Cl_2 \xrightarrow[h\nu\ (HELP)]{\text{sunlight}} \dot{C}C + \dot{C}C$ (Homolytic cleavage)

8) Compare C-H bond energies in the following molecules.



Stability : b > a > d > c

$BE \propto \frac{1}{\text{stability}}$ ∴ BE : b < a < d < c

Q) 1st intermediate is more stable than second

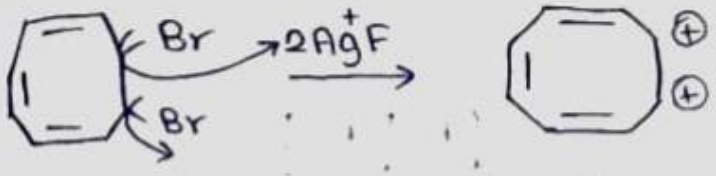
$CH_3-CH=\overset{\oplus}{C}H < CH_2=CH-\overset{\oplus}{C}H_2$

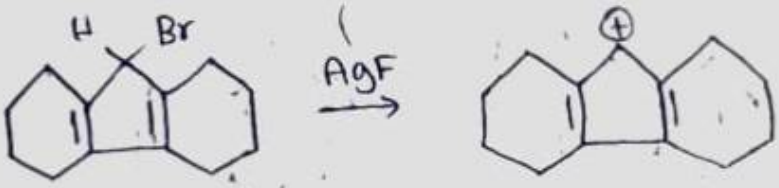
$CCl_3^{\ominus} \geq CF_3^{\ominus}$

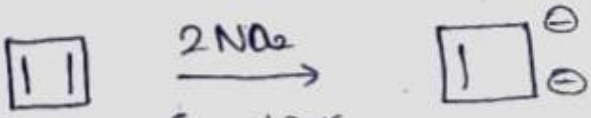
⊛ Hyperconjugation ethyl cation involves overlapping of $C_{sp^2}-H_{1s}$ bond with empty 2p orbital of other carbon.

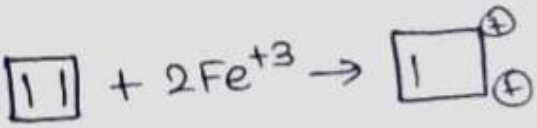
$CH_3-\overset{\oplus}{C}H_2$
sp^3

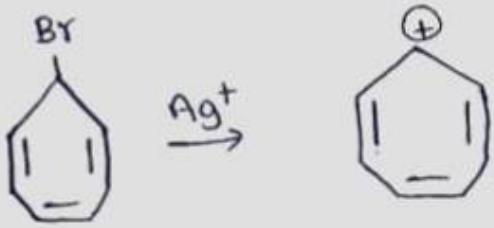
Q) which of the following rxns give aromatic product ?



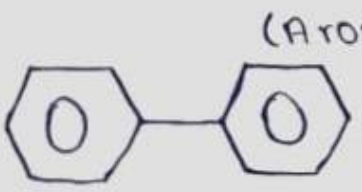




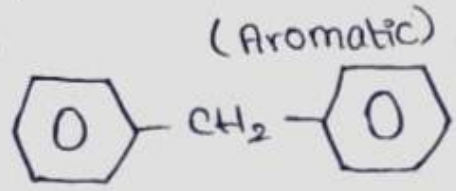




Q) Aromatic compounds ?

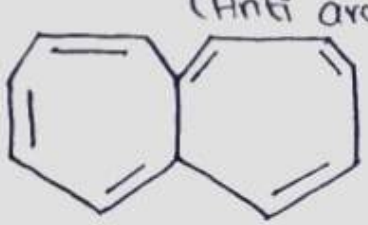


(Biphenyl)



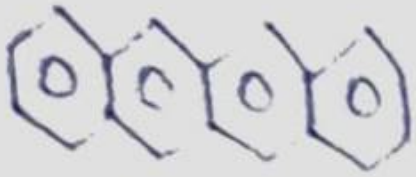
(Diphenyl methane)

(pentalene)



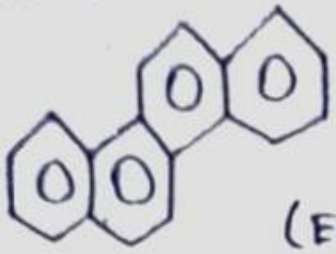
(Heptalene)

$F_3N_2H_2$ (Benzene) (Aromatic)



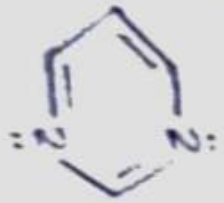
(Tetracene)

(Aromatic)



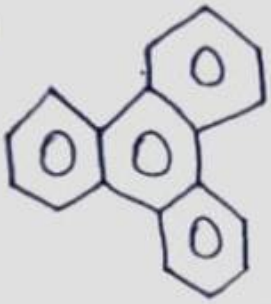
(Fryfene)

(Aromatic)



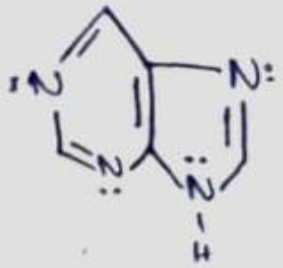
(Pyramidine)

(Aromatic)



(Tetraphenylene)

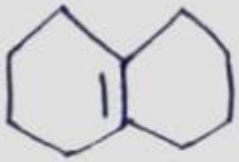
(Aromatic)

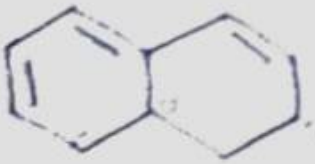


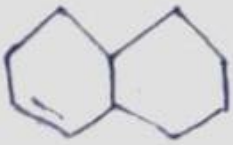
(purine)

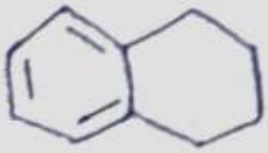
(Aromatic)

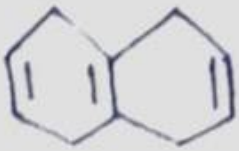
*) No. of compounds having higher Heat of ~~hydration~~ hydrogenation than







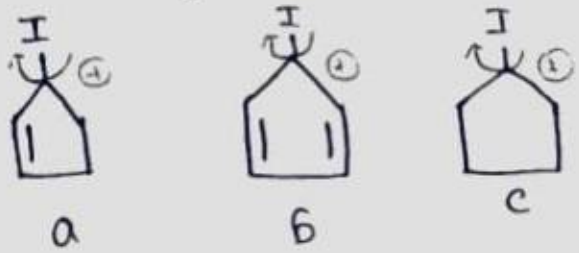




Ans : 7

With increase in no. of double bonds, heat of hydrogenation increases.

Q) Rate of abstraction of I^- by Ag^+ is

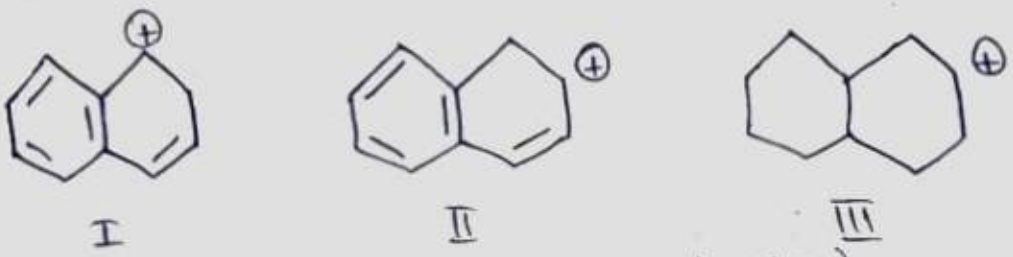


a b c

*) a > c > b

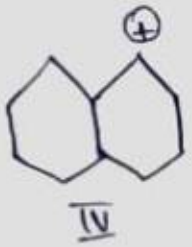
Q) Stability order :

i)



I II III

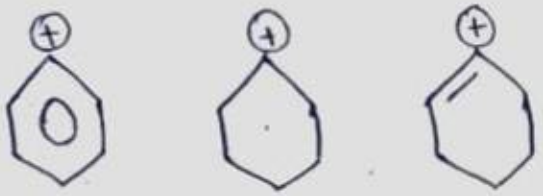
(continuous conjugation)



IV

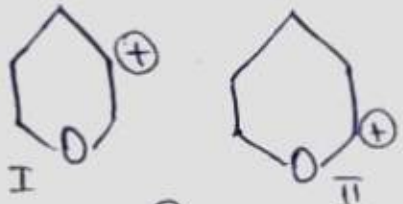
(II > I > III > IV)

ii)



(II > III > I)

iii)

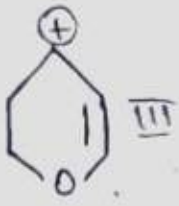


I II

iv)

I

II



III

(III > II > I)

III

IV

: (III > II > I > IV)

(*)

$10\pi e^{\ominus}$

(Aromatic)

*) Overall stability of free radicals :

$Ph_3\dot{C} > Ph_2\dot{C}H > (CH_3)_3\dot{C} > Ph\dot{C}H_2 >$

$CH_2=CH-\dot{C}H_2 > (CH_3)_2\dot{C}H > CH_3-\dot{C}H_2 > \dot{C}H_3 >$

$CH_2=\dot{C}H > HC\equiv\dot{C}$

Compare stability :

*) $CH_2=CH-\dot{C}H_2$ > $CH_3-CH_2-\dot{C}H_2$

(Allyl) (1°)

*)

(Allyl) (Allyl)

*) $\dot{C}H_2=\dot{C}H$ (a) , $\dot{C}H_2=CH-\dot{C}H_2$ (b)

(c) (1°)

(d) (3° Allyl)

Stability : d > b > c > a

*)

(Phenyl) (a)

(Allyl) (b)

(c) (Vinyl)

(d)

(Allyl)

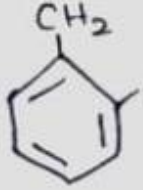
(e)

(2°)

Stability : b > d > e > c > a

*) (a)

(b) CH_3 (+I)

 CH_3 (+I, HC) (c)

(d) (+I, HC)

Stability : c > d > b > a

*) (a) NO_2 (−I, −M)

(b)

(c) NO_2 (−I, −M)

(d)

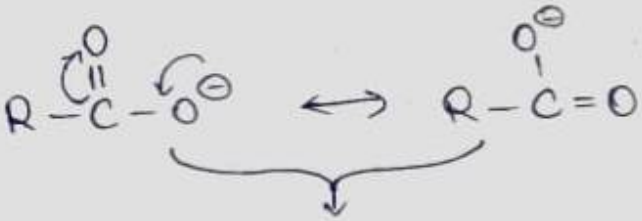
Stability :

d > b > a > c

*) Acidic strength of carboxylic acids :

$$R-\overset{O}{\overset{\|}{C}}-O-H \rightarrow R-\overset{O}{\overset{\|}{C}}-O^{\ominus} + H^{\oplus}$$

(carboxylic acid) (carboxylate ion) (conjugate base)



Equivalent resonating structures

Stability is more for $RCOO^{\ominus}$ than RCOOH.

*) Acidic strength of RCOOH :

α stability of $RCOO^{\ominus}$; α −I ;

α −M ; $\alpha \frac{1}{+I}$; $\alpha \frac{1}{+M}$; α K_a

$\alpha \frac{1}{pK_a}$

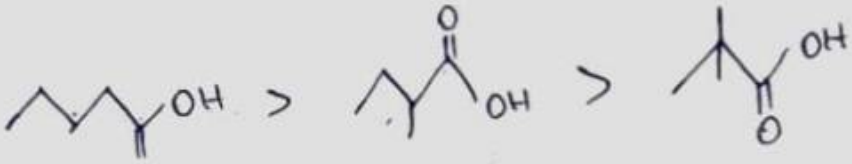
Compare the acidic strength of acids

*) $HCOOH > CH_3COOH > CH_3CH_2COOH$

*) $Ph-\overset{\overset{O}{\|}}{C}-OH > CH_3COOH$

*) $HCOOH > PhCOOH$ (Due to equivalent resonating structures of formate ion)

*) $HCOOH > Ph-COOH > CH_3-COOH$
(-I, +M) (+I)

*) 

*) $CH_3COOH < \underset{\underset{Cl}{|}}{CH_2}-COOH < CHCl_2COOH < CCl_3COOH$

*) $\underset{\underset{F}{|}}{CH_2}-COOH > \underset{\underset{Cl}{|}}{CH_2}-COOH > \underset{\underset{Br}{|}}{CH_2}-COOH > \underset{\underset{I}{|}}{CH_2}-COOH$

*) $\underset{\underset{NO_2}{|}}{CH_2}COOH > \underset{\underset{CN}{|}}{CH_2}COOH > \underset{\underset{Cl}{|}}{CH_2}COOH > \underset{\underset{OH}{|}}{CH_2}COOH$

*) $CH_3COOH > CD_3COOH$

*) $CH_3CH_2COOH < CH_2=CH-COOH < HC\equiv C-COOH$

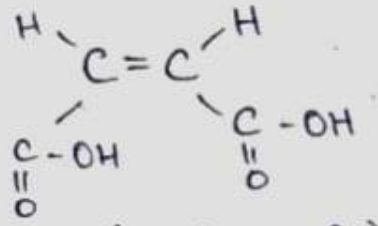
*) $F-CH_2-COOH > \underset{\underset{CH_3}{|}}{Cl-CH}-CH_2COOH > F(CH_2)_2COOH > Br(CH_2)_2COOH$

*) $\underset{\underset{COOH}{|}}{COOH}$ (Oxalic acid) $> CH_2\begin{matrix}-COOH \\ \diagdown COOH\end{matrix}$ (Malonic acid) $> \underset{\underset{CH_2-COOH}{|}}{CH_2-COOH}$ (Succinic acid) $> CH_2\begin{matrix}-CH_2-COOH \\ \diagdown CH_2-COOH\end{matrix}$ (Glutaric acid) >

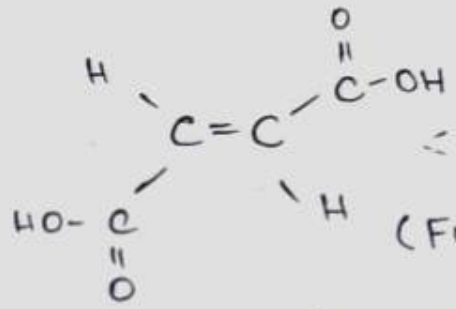
CH_2-CH_2-COOH

CH_2-CH_2-COOH

(Adipic acid)

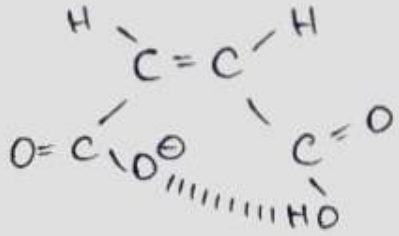
*) 

(Maleic acid)

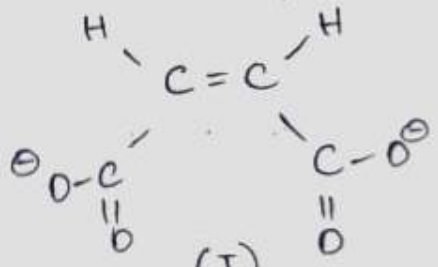


(Fumaric acid)

$Ka_1 \downarrow -H^{\oplus}$

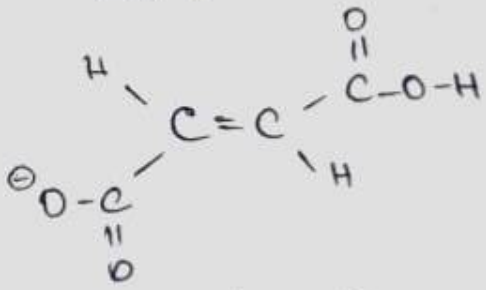


$Ka_2 \downarrow -H^{\oplus}$

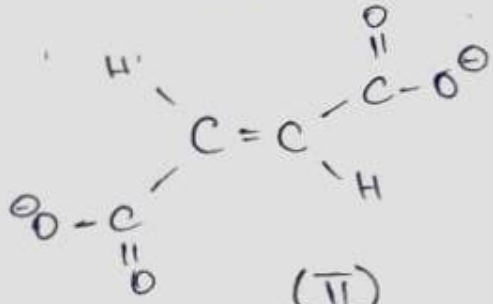


(I)

$Ka_1' \downarrow -H^{\oplus}$



$Ka_2' \downarrow -H^{\oplus}$



(II)

$Ka_1 > Ka_1'$

Stability : II > I

$\Rightarrow Ka_2' > Ka_2$

*) Acidic strength of alcohols (R-O-H):

$R-O-H \longleftrightarrow R-O^{\ominus} + H^{\oplus}$

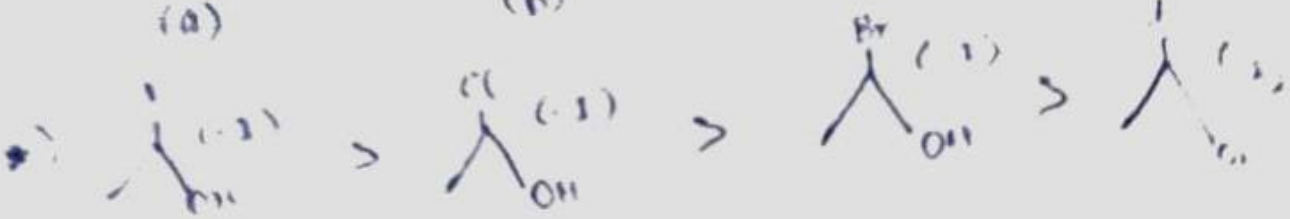
(Alcohol) (Alkoxide ion)

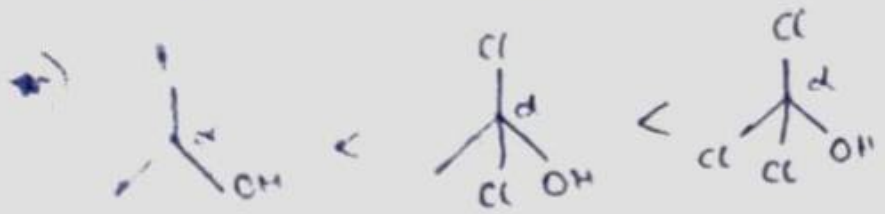
Acidic strength of alcohol $\propto$ Alkoxide ion stability.

α-I $\propto \frac{1}{pKa}$ α-M $\propto \frac{1}{+I}$

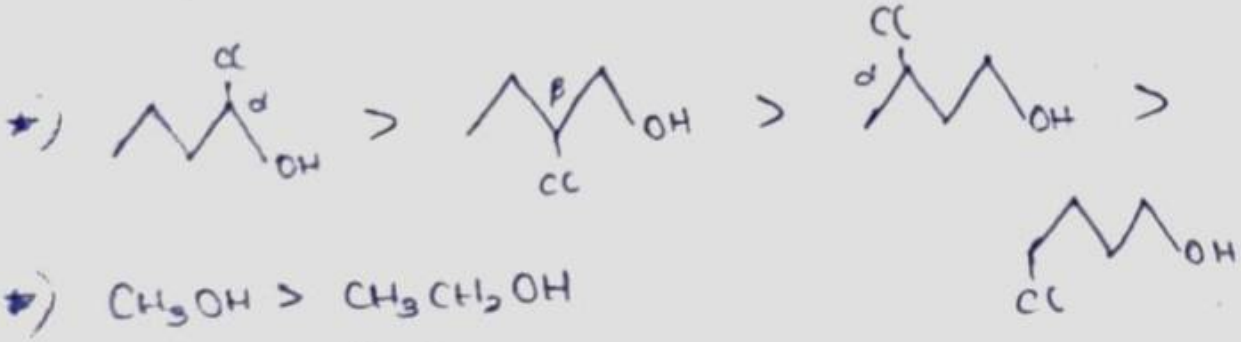
$\propto \frac{1}{+M}$ $\propto Ka$

*)
(A) (B) (C)

*) 

*) 

*) CH_3-OH > CH_3-CN > CH_3-OH
NO_2 (-I) OH (-I) NH_3 (-I)

*) 

*) CH_3OH > CH_3CH_2OH
(+I) (+I)

*) CH_3OH > CD_3OH
(+I) (+I)

*) CCl_3-CH < CF_3-OH
(-I) (I)

*) CH_3-CH_2-OH < $CH_2=CH-OH$ < $HC\equiv C-OH$
sp^3 sp^2 (sp)

Acidic strength:

R-COOH > R-OH (Due to equivalent resonating structures of carboxylate ion)

CH_3COOH > CH_3CH_2OH

*) Acidic strength of phenols:

(phenoxide ion)

Acidic strength of $ph-OH$ $\propto$ Stability of $ph\,O^{\ominus}$

$\propto -I$ $\propto K_a$ $\propto \frac{1}{K_a}$ $\propto -M$ $\propto +I$ $\propto \frac{1}{+M}$

Acidic strength:

$R-\overset{\overset{O}{\|}}{C}-OH$ > $ph-OH$

$R-\overset{\overset{O}{\|}}{C}-O^{\ominus}$ > $ph-O^{\ominus}$ (Stability)

(2RS) (5RS)

(Equivalent RS)

Acidic strength:

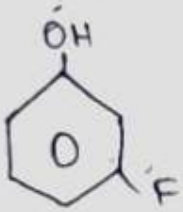
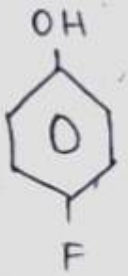
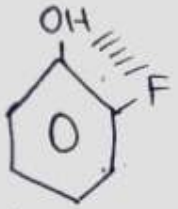
$ph-OH$ > $R-OH$

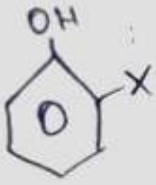
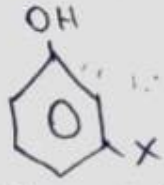
*) Acidic strength:

*) > >

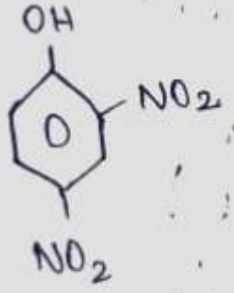
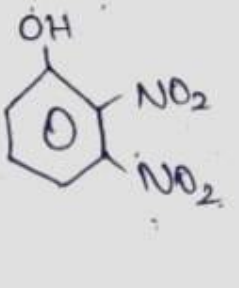
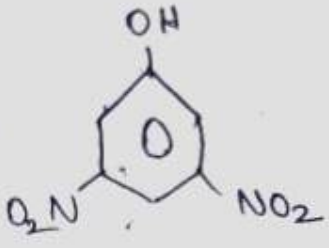
(-I, +M)

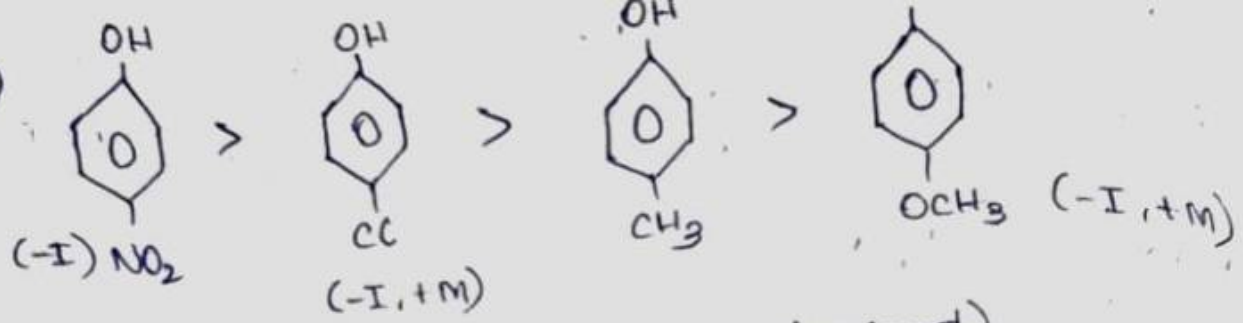
(-I, -M)

*)  >  > 

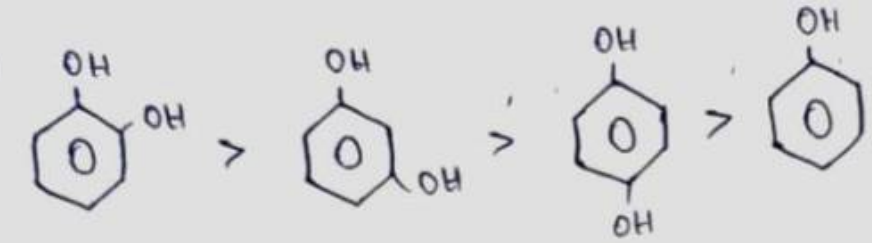
*)  >  >

(X = Cl, Br, I)

*)  >  > 

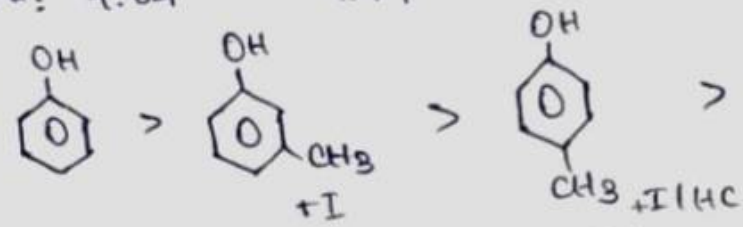
*) 

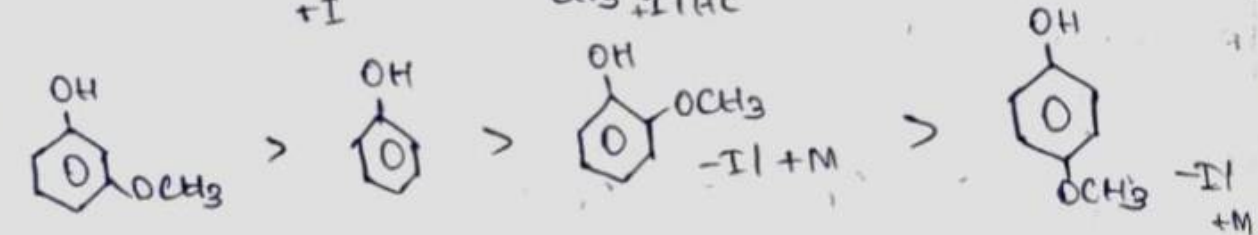
(Halogens, inductive effect is dominant)

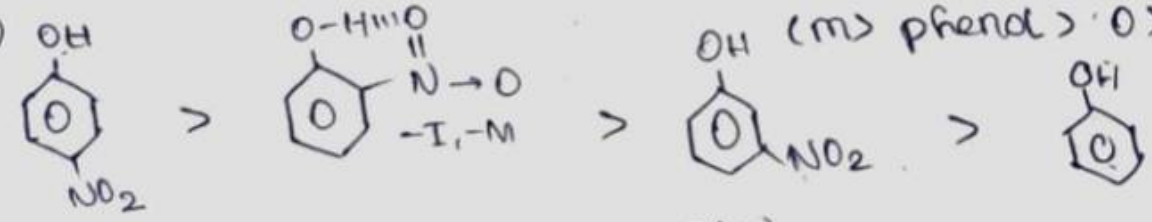
*) 

(Acidic strength)

pKa: 9.84 9.94 9.96 9.98

*) 

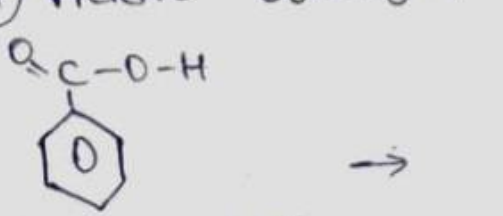
*) 

(*) 

(m> phenol > o > p)

(para nitro phenol is more acidic)

(*) Acidic strength of Benzoic acid:



Benzoic acid (phCOOH)

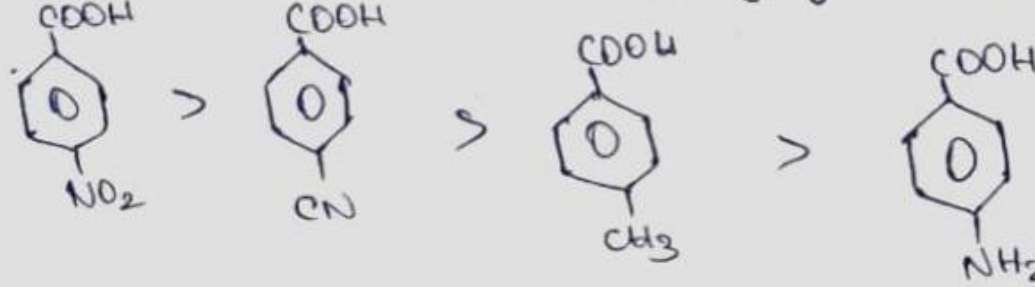
Benzoate ion (phCOO⁻) (conjugate base)

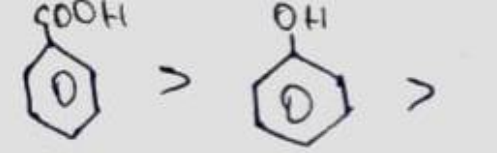
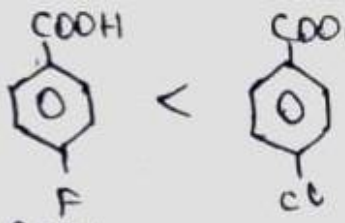
α -I : α Ka

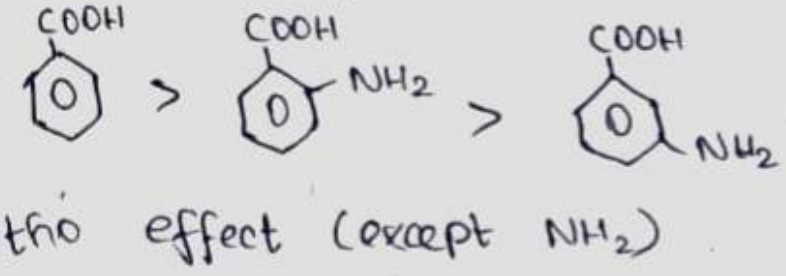
α -M ; $\alpha \frac{1}{+I}$

$\alpha \frac{1}{pKa}$

$\alpha \frac{1}{+M}$

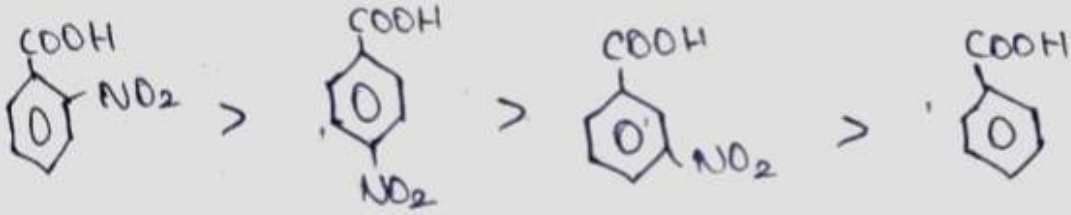
* 

(*)  ; (*) 

(*)  (Vacant d-orbital)

, Ortho effect (except NH_2)

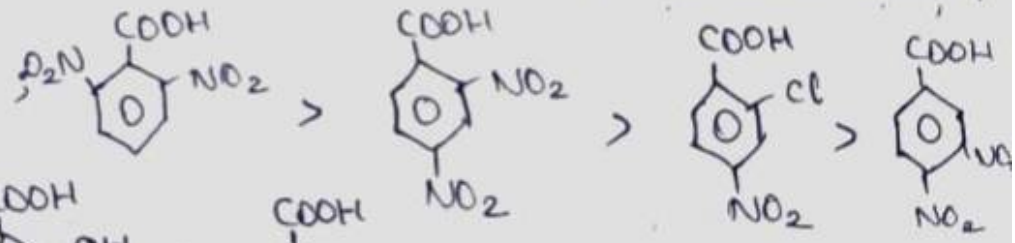
Ortho substituted benzoic acids are more acidic than meta & para isomers and also more acidic than benzoic acid.

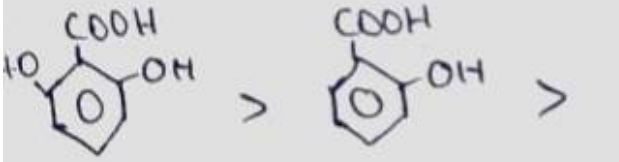


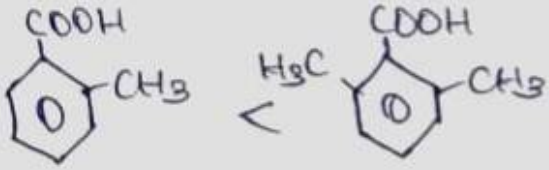
In CH_3,

O > Benz. acid > m > p ; In OCH_3, O > m > benz. acid > p

In X,

O > m > p 

 (H.C → less acidic)

 (No need to consider steric / H-bond during o-effect)

) Acidic strength of hydrocarbons: & stability of conjugate base

CH_3-CH_3 < $CH_2=CH_2$ < $CH\equiv CH$

sp^3 sp^2 sp

CH_4 (I) CH_3-CH_3 (II) $CH_3-CH_2-CH_3$ (III) $CH_3-\underset{CH_3}{\overset{CH_3}{CH}}-CH_3$ (IV)

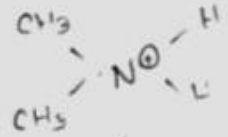
$\downarrow -H^+$ $\downarrow -H^+$ $\downarrow -H^+$ $\downarrow -H^+$

$CH_3^{\ominus}$ $CH_3-CH_2^{\ominus}$ $CH_3-\overset{\ominus}{C}H-CH_3$ $CH_3-\overset{\ominus}{\underset{CH_3}{C}}-CH_3$

I > II > III > IV

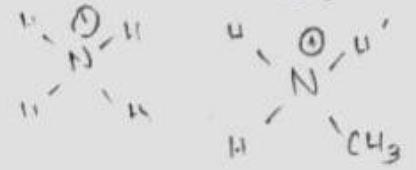
*) Basic strength of amines:

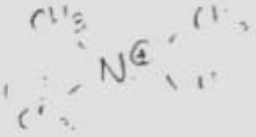
*) Basic strength:



$NH_3 < CH_3NH_2 < (CH_3)_2NH < (CH_3)_3N$

(1°) (2°) (3°)





→ No. of CH_3 groups ↑

Stability ↑

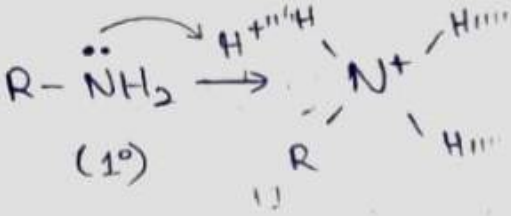
conjugate acid

α +I : α +M

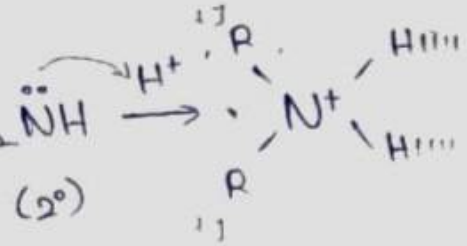
$\alpha \frac{1}{-I} : \alpha \frac{1}{-M}$

$\alpha K_b : \alpha \frac{1}{pK_b}$

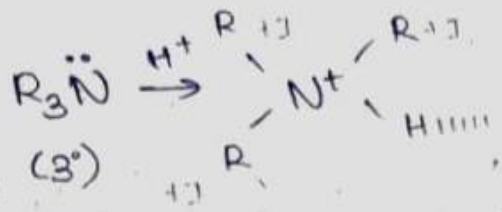
*) In aqueous medium:



(1°)



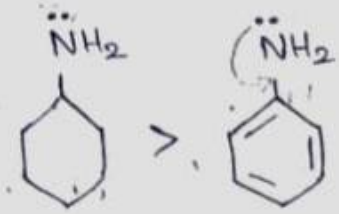
(2°)



(3°)

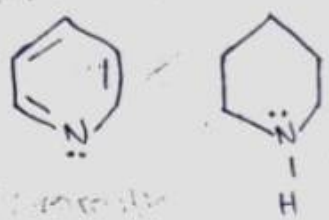
(Basic strength : 2° > 1° > 3° (R = $-CH_3$)

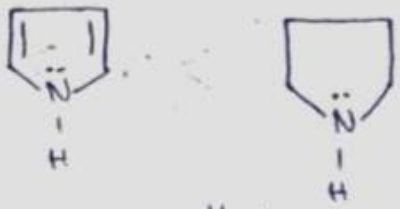
: 2° > 3° > 1° (R = $-C_2H_5$))

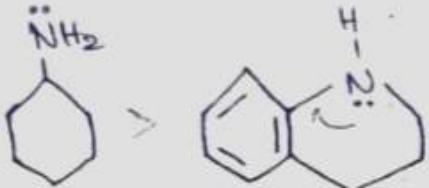
*) 

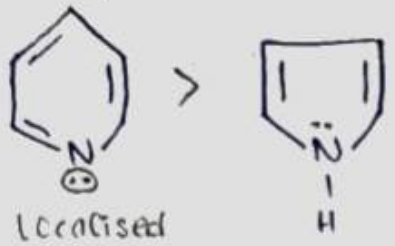
→ Involved in delocalization (Basic strength is less)

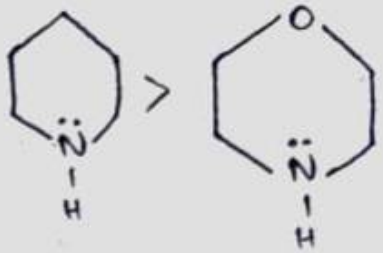
(Aliphatic) (Aromatic)

*) 

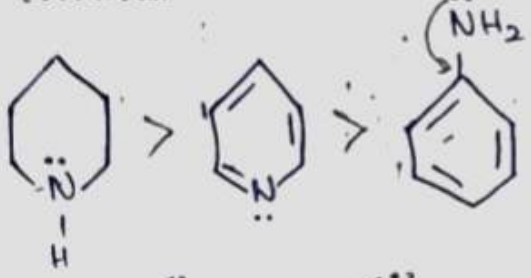
*) 

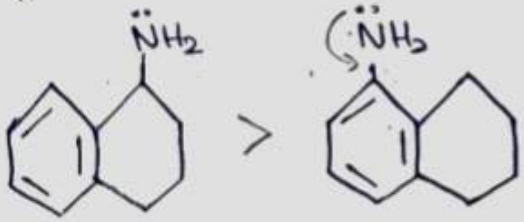
*) 

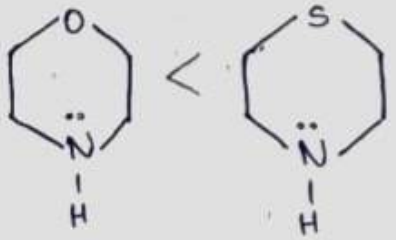
★)  Localised

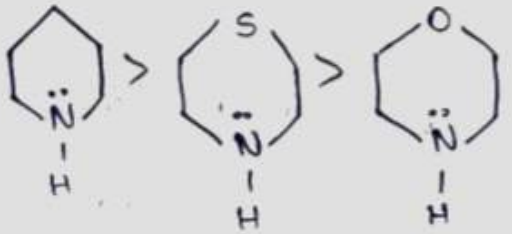
★) 

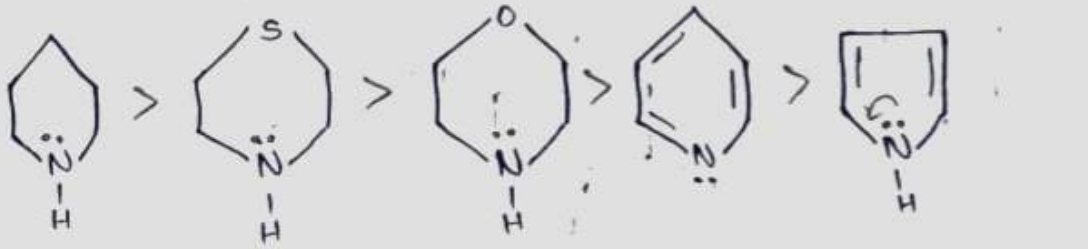
Basic strength $\propto \frac{1}{EN}$

★)  → Lone pair should be involved in delocalization

★) 

★) 

★) 

★) 

★) $CH_3CH_2NH_2 > CH_2=CH-NH_2 > HC\equiv C-NH_2$

sp^3 sp^2 sp

★) $R-\ddot{N}H_2 > R-CH=NH > R-C\equiv N$

sp^3 (Amine) sp^2 (Imine) sp (cyanide)

% S ↑

EN ↑

Basic strength ↓

★) $CH_3-CH_2-NH_2 > CH_3-\overset{O}{\overset{\|}{C}}-\ddot{N}H_2$

(Amine) (Amide)

★) $CH_3-\overset{O}{\overset{\|}{C}}-\ddot{N}H_2 < ph-\overset{O}{\overset{\|}{C}}-\ddot{N}H_2$ → localized

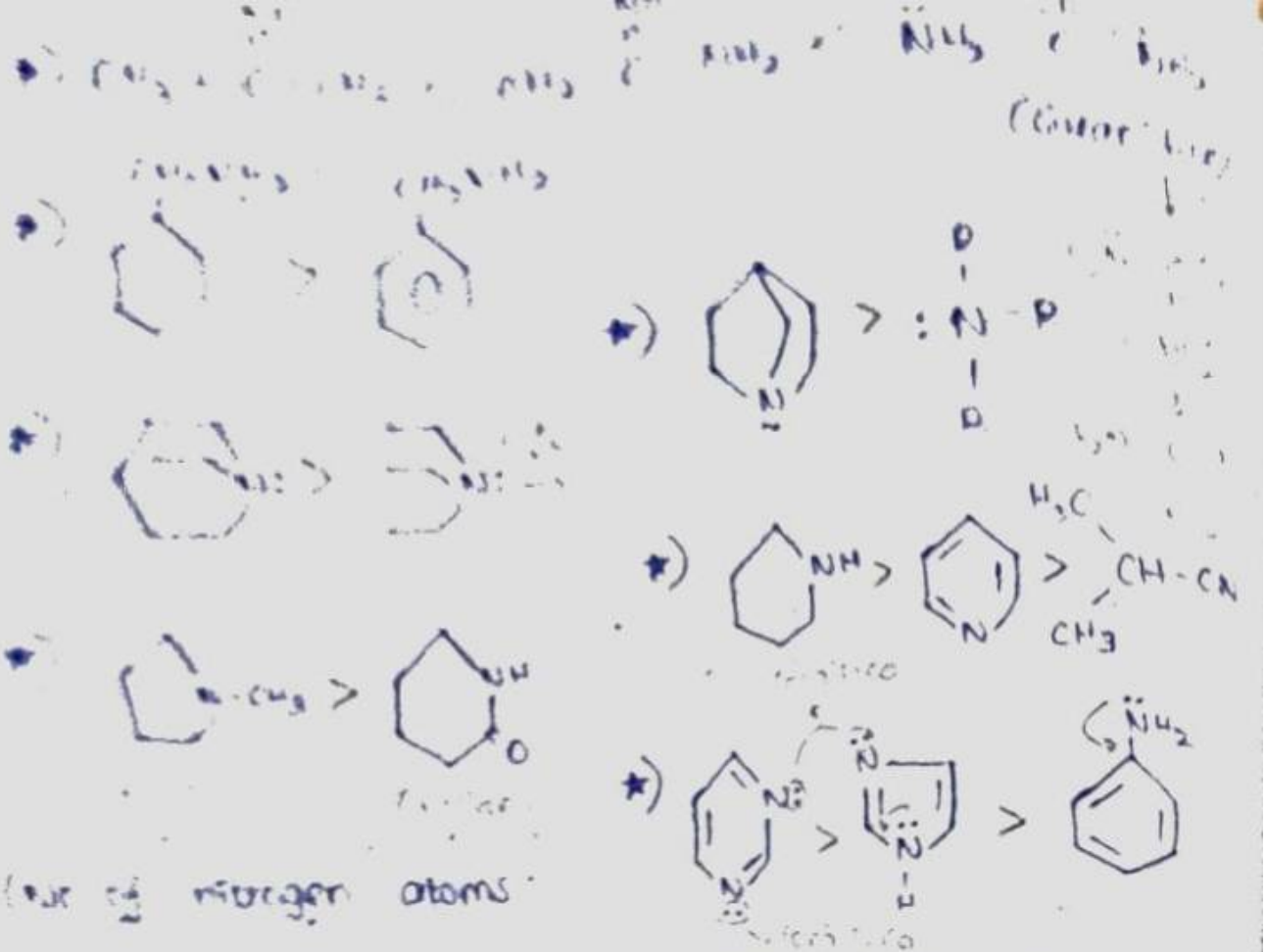
(Acetamide) (Benzamide)

★) $CH_3-\overset{O}{\overset{\|}{C}}-\ddot{N}H_2 < \ddot{N}H_2-\overset{O}{\overset{\|}{C}}-\ddot{N}H_2$ (Urea)

(1°) (2°) (3°)

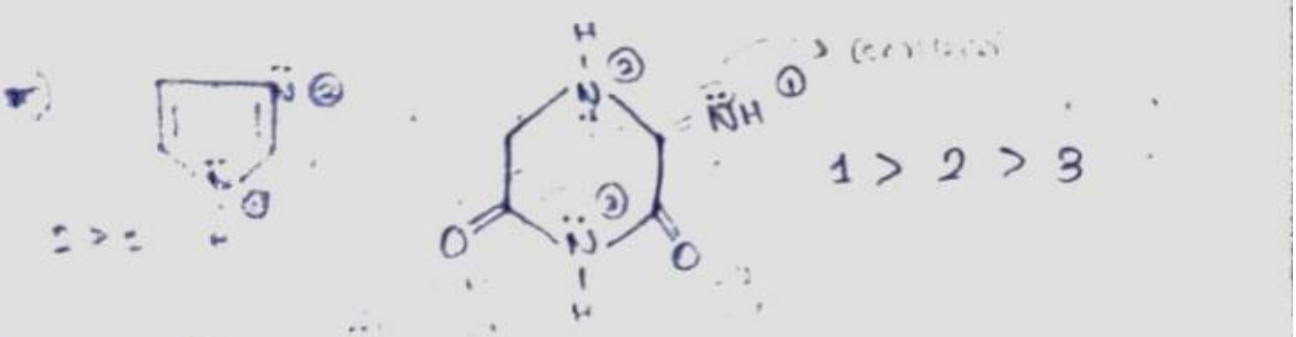
(No. of N atoms involved in conjugation 1)

★) $phNH_2 > ph_2NH > ph_3N$ (More delocalization, less basic strength)

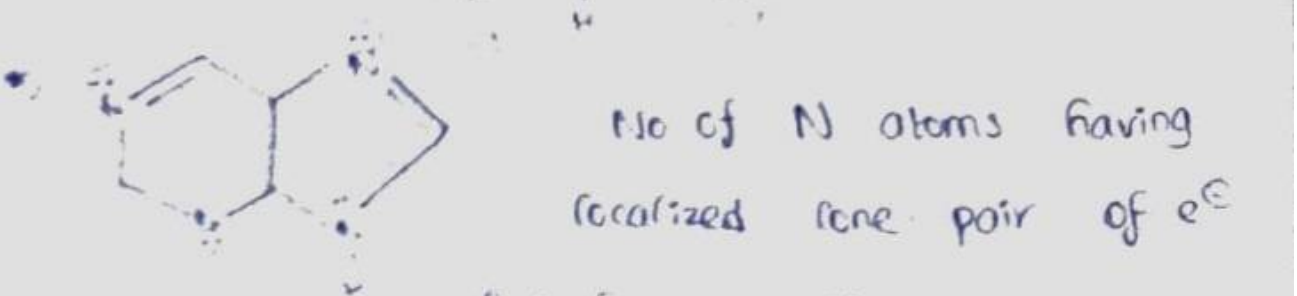


(for N nitrogen atoms

increased in conjugation ↑, ~~sta~~ basic strength ↑)

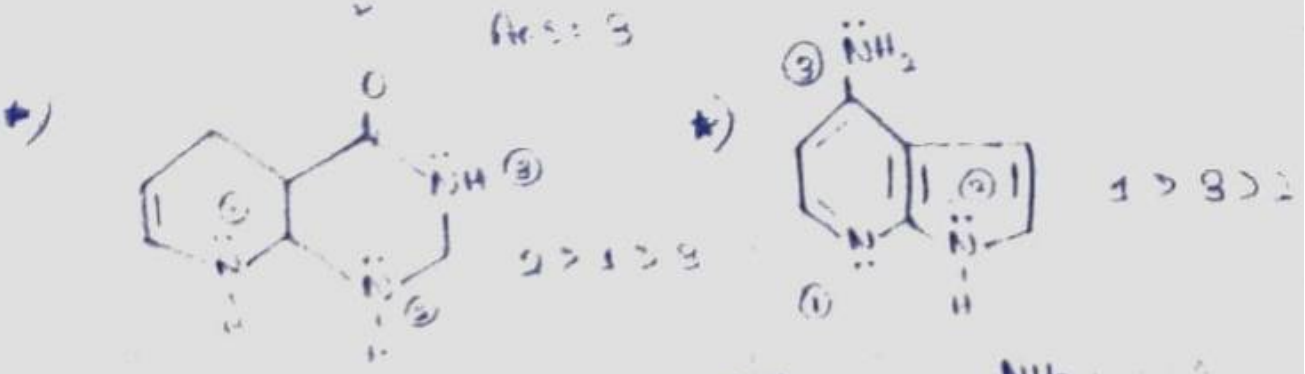


1 > 2 > 3



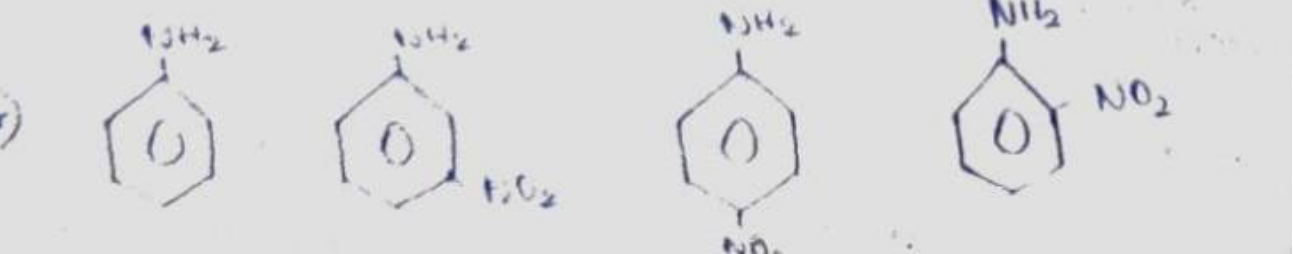
No of N atoms having localized lone pair of $e^{\ominus}$

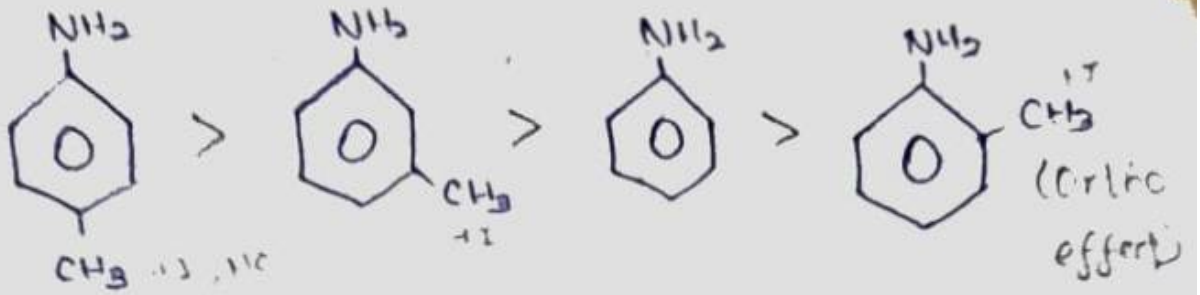
Ans: 3

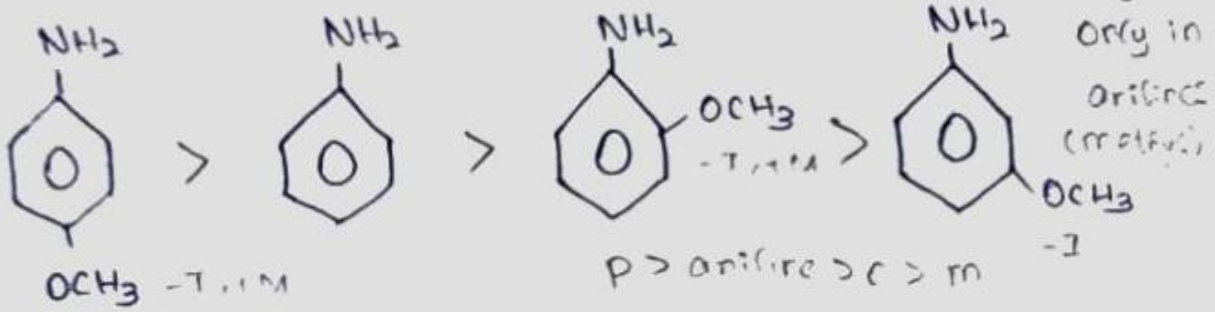


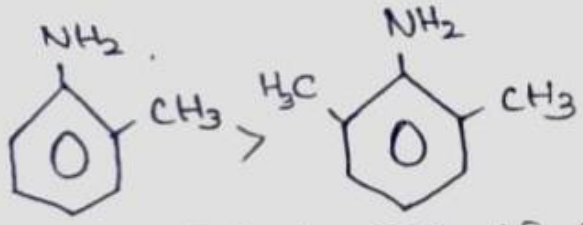
2 > 1 > 3

1 > 3 > 2

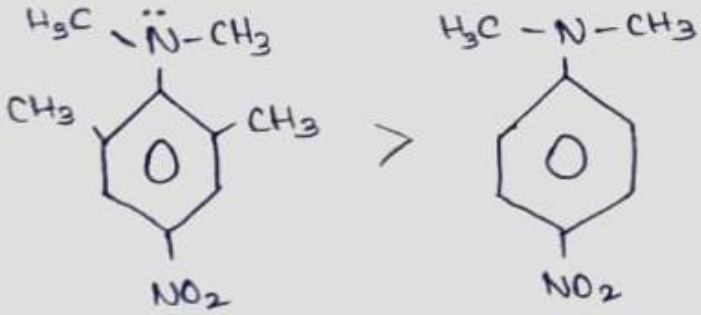


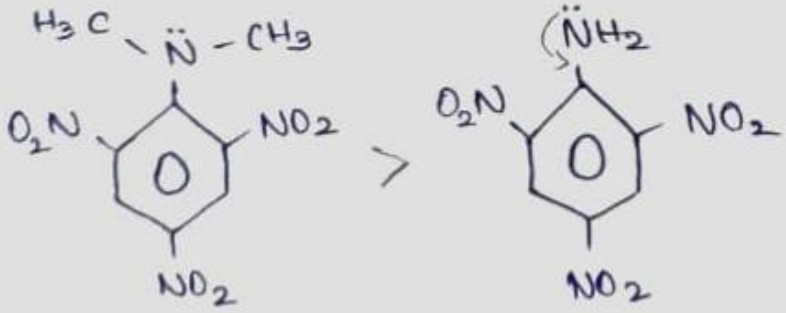
(★) 

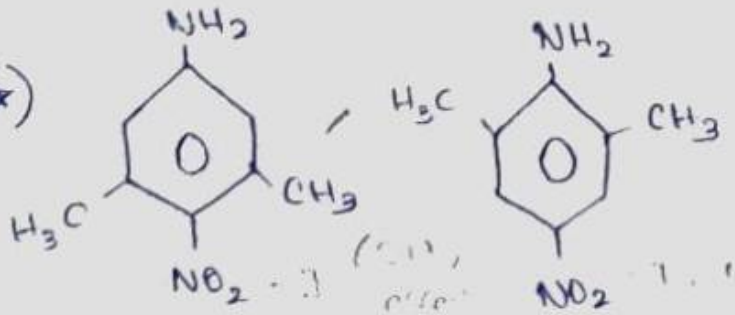
(★) 

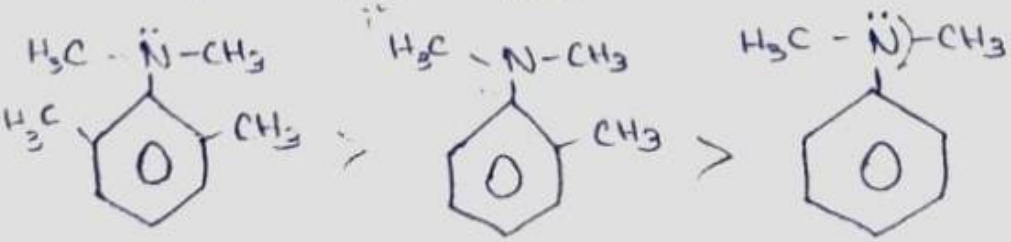
(★) 

→ Due to SIP, LP is not involved in resonance

(★) 

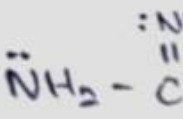
(★) 

(★) 

(★) 

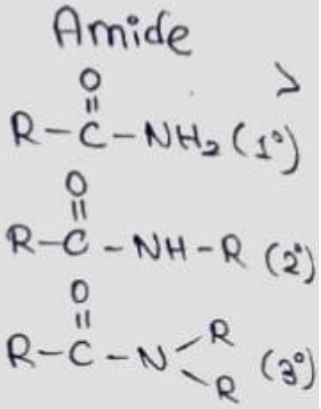
*) Overall basic strength :

Guanidine > Aliphatic amines > NH_3 >



(3° > 2° > 1°)

Aromatic amines > Imines > Amide >

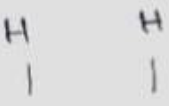


Cyanides (R-CN)

*) Carbene :

Carbenes are divalent neutral species having lone pair of $e^{\ominus}$.

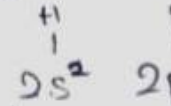
These are $e^{\ominus}$ deficient compounds and act as electrophiles.



GSEC of C : $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^0$

sp^2

ESEC of C :



$1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$

Singlet carbene

Diamagnetic

sp^2, 1LP, Angular

Bent / V-shape

$\Sigma S = +\frac{1}{2} - \frac{1}{2}$

$= 0$

Triplet carbene

sp, linear, paramagnetic

Spin multiplicity : $2(\Sigma S)+1 \Rightarrow 2(0)+1 \Rightarrow 1$

$S = -\frac{1}{2} + \frac{1}{2} = 1$

Spin multiplicity - $2(S)+1 \rightarrow 2(1)+1 \rightarrow 3$

Triplet carbene is more stable than singlet carbene.

$:CX_2 \rightarrow$ Dihalo carbene

They exist only in singlet state due to back bonding.

Effective back bonding order

Stability-: $:CF_2 > :CCl_2 > :CBr_2 > :CI_2$

$2p\text{-}2p \quad 2p\text{-}3p \quad 2p\text{-}4p \quad 2p\text{-}5p$

*) Generation of carbene:

*) $CH_2N_2 \xrightarrow{h\nu} :CH_2 + N_2\uparrow$

(Diazo methane)

*) $CH_2=C=O \xrightarrow{h\nu} :CH_2 + CO\uparrow$

(Ketene)

*) $CHX_3 \xrightarrow{\text{alc. KOH}} :CX_2 + H_2O + KX$

(Trihalo methane)

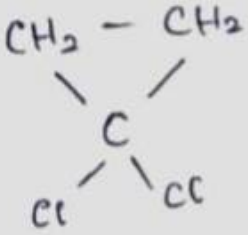
*) $CHCl_3 \xrightarrow{\text{alc. KOH}} :CCl_2 + KCl + H_2O$

(Chloroform)

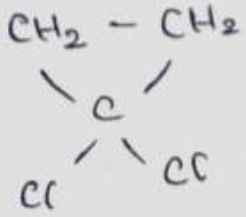
*) $CHCl[Br] \xrightarrow[\text{alc. KOH}]{\text{alc. KOH}} :CClBr + H_2O + KI$

*) Properties of carbene :

1) Reaction with alkenes :-

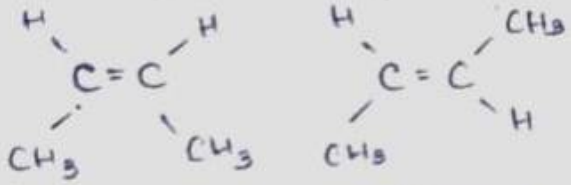
$CH_2 = CH_2 \xrightarrow[\text{alc. KOH}]{CHCl_3}$ 

$CHCl_3 \xrightarrow{\text{alc. KOH}} :CCl_2$

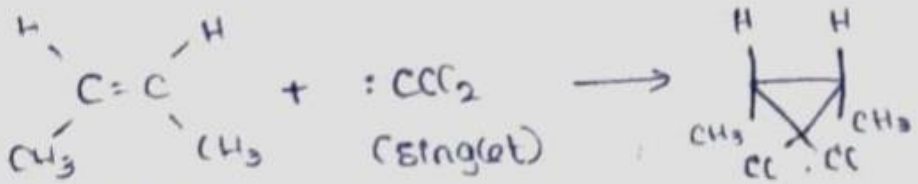
$CH_2 = CH_2 \longrightarrow$ 

2) $CH_3 - CH = CH - CH_3 \xrightarrow[\text{alc. KOH}]{CHCl_3}$

2-Butene

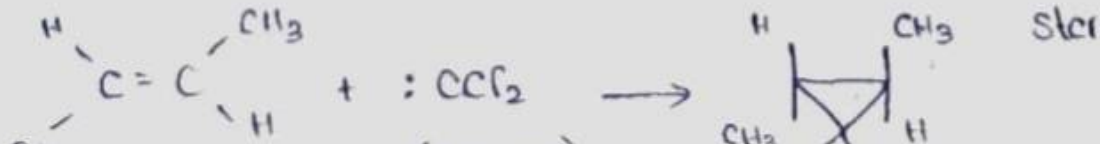


(cis) (Trans)

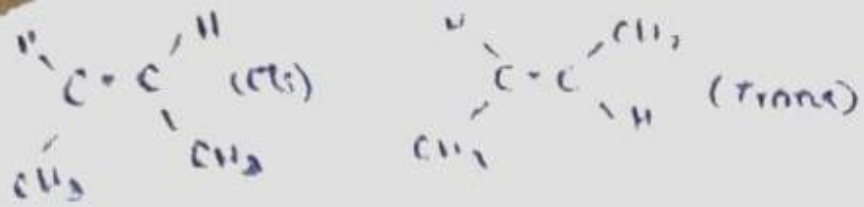


(cis) (Singlet) (cis)

Stereo selective and stereo specific reaction



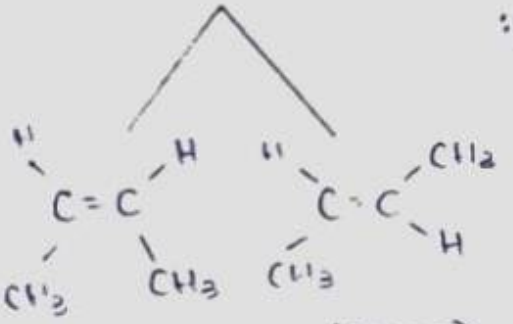
(Trans) (Singlet) (Trans)



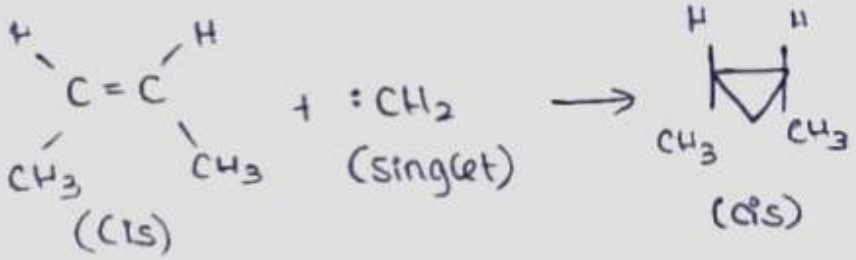
*) $CH_3 - CH = CH - CH_3 \xrightarrow[h\nu]{CH_2N_2}$

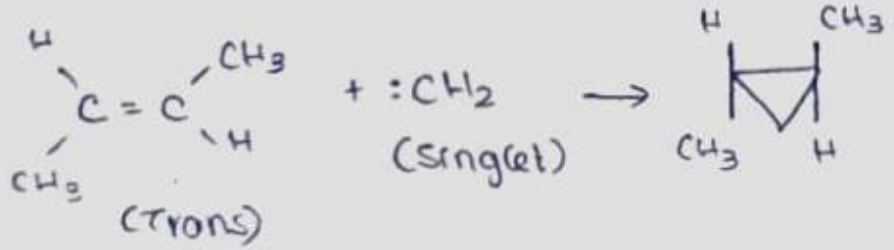
(2-Butene)

$:CH_2$

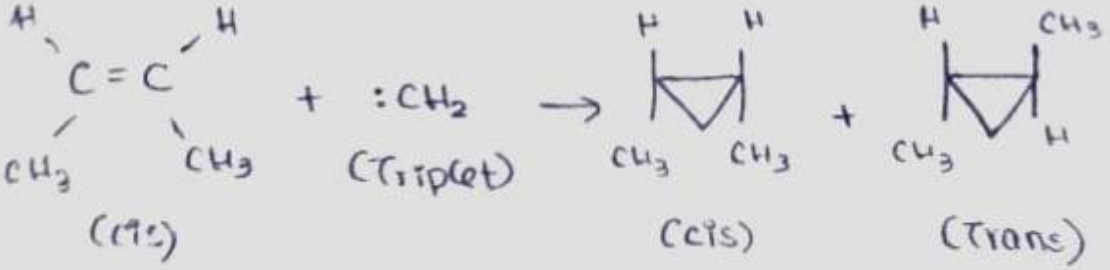


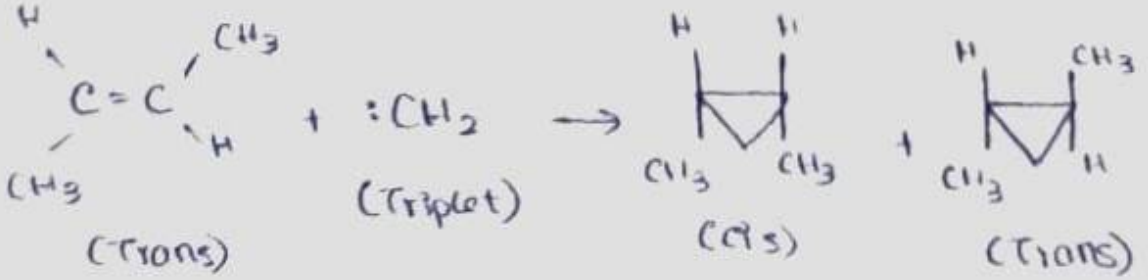
(Cis) (Trans)





Stero selective v stereo specific reaction





9) Reaction with alkanes:

*) $CH_4 \xrightarrow[h\nu]{CH_2N_2\ /} CH_3 - CH_3$

$CH_3 - H$ $(:CH_2)$

*) $CH_3 - CH_3 \xrightarrow[h\nu]{CH_2N_2\ /} CH_3 - CH_2 - CH_3$

$CH_2 - CH_2$ $(:CH_2)$

*) $CH_3 - CH_2 - CH_3 \xrightarrow[h\nu]{CH_2N_2\ /} CH_3 - CH_2 - CH_2 - CH_3 +$

$CH_3 - CH(CH_3) - CH_3$

$CH_2 - CH - CH_2$ $(:CH_2)$

4) Reaction with alcohols :

*) $CH_3 - O - H \xrightarrow[h\nu]{CH_2N_2\ /} CH_3 - CH_2 - OH + CH_3 - O - CH_3$

$CH_2 - O - H$ $(:CH_2)$

*) $CH_3 - CH_2 - O - H \xrightarrow[h\nu]{CH_2N_2\ /} CH_3 - CH_2 - CH_2 - OH +$

$CH_3 - CH(CH_3) - OH +$

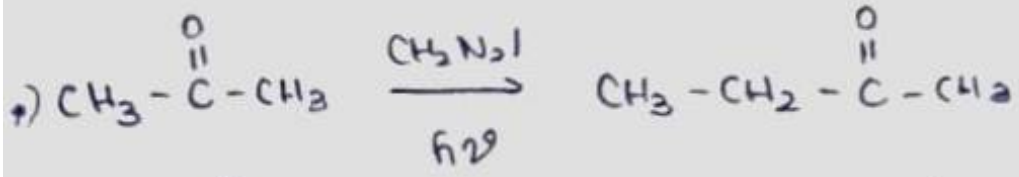
$CH_2 - CH - O - H$ $(:CH_2)$

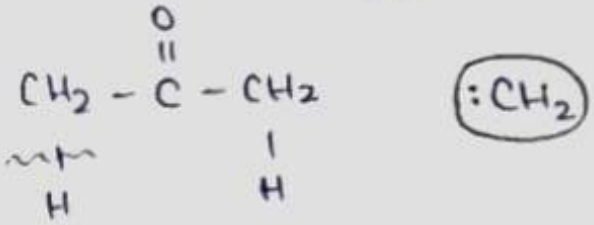
$CH_3 - CH_2 - O - CH_3$

5) Reaction with aldehyde :

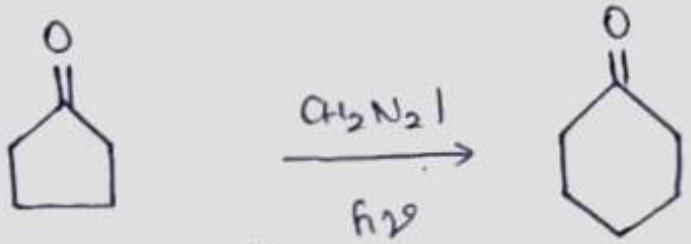
$CH_3 - C(=O) - H$ (Aldehyde) $\xrightarrow[h\nu]{CH_2N_2\ /} CH_3 - C(=O) - CH_3 + CH_3 - CH_2 - C(=O) - H$

6) Reaction with Ketones:



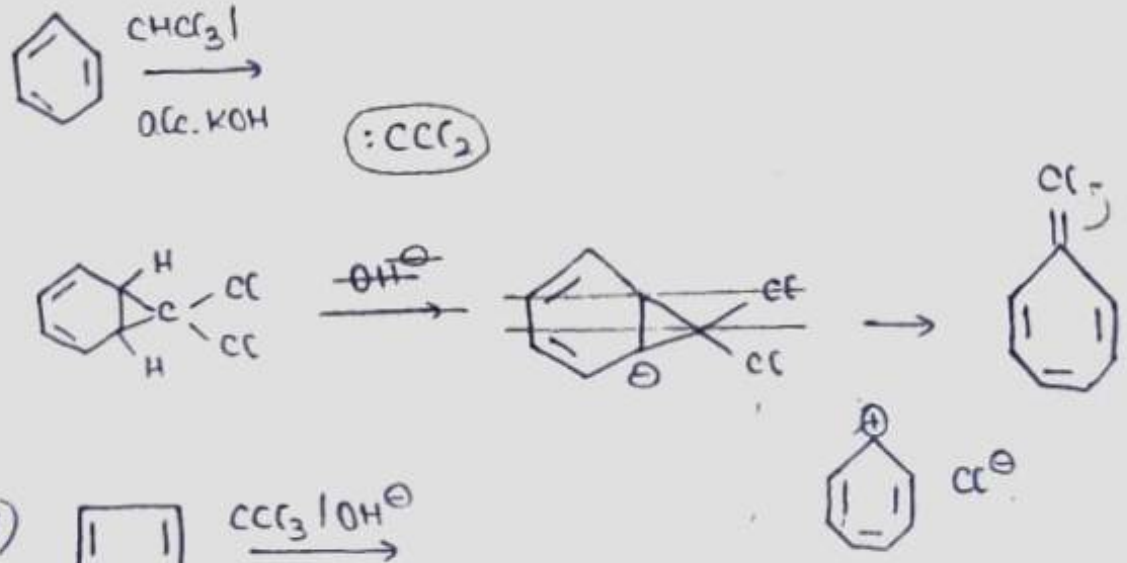


*)

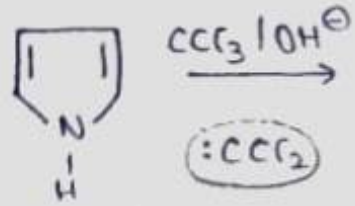


(Cyclo pentanone)

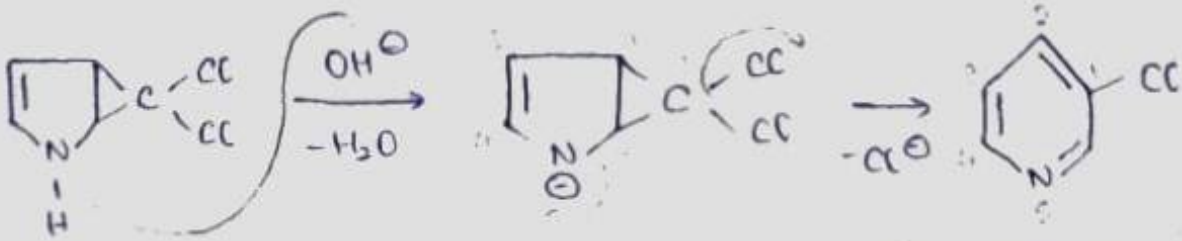
*)



*)



(pyrrole)



(3 - chloro pyridine)

Carbenes are highly reactive intermediates of carbon.

*) Nitrenes :

Nitrenes are neutral monovalent species having 2 lone pair of $e^{\ominus}$.

Nitrenes also exist in singlet & triplet states and properties of nitrenes are similar to carbenes.

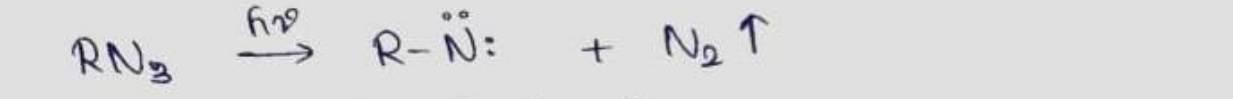
(Nitrene) (Acyl nitrene) (Acyl nitrene)

Nitrenes are highly reactive intermediates of nitrogen. These are $e^{\ominus}$ deficient species and act as electrophiles.

Nitrenes are more reactive than carbenes.

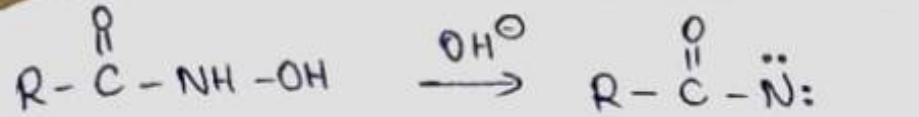
*) Generation of nitrenes :

(Hydrozoic acid)

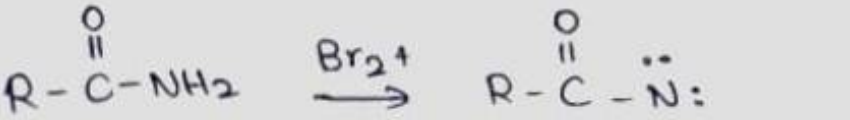


(Acyl azide) (Acyl nitrene)

(Acyl iso cyanate)



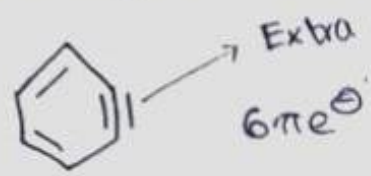
(Hydroxamic acid) (Acyl nitrene)



(Amide) (Acyl nitrene)

(Acyl azide) (Acyl nitrene)

*) Benzyne :

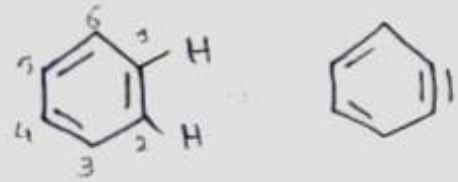


(Benzyne)

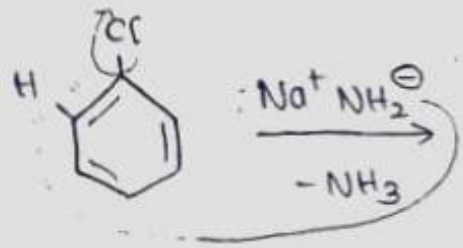
(Aromatic)

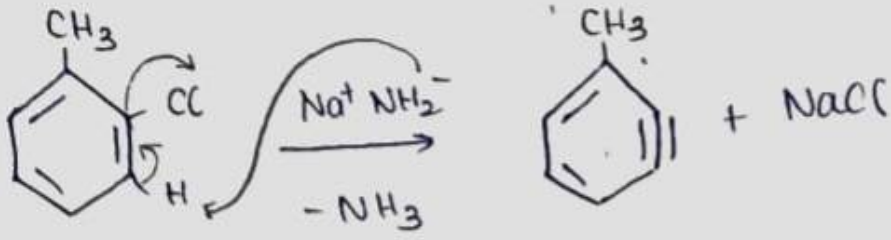
poor sp^2 overlapping of two carbon atoms

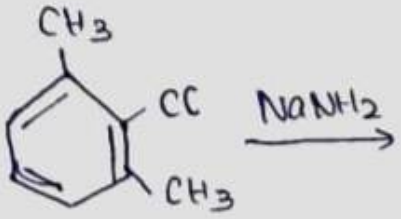
IUPAC : 1,2 - dedihydro ~~didehydro~~ benzene



*) Generation of benzyne :



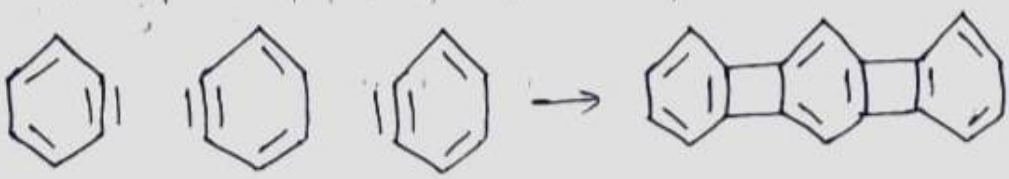




No Benzyne formation

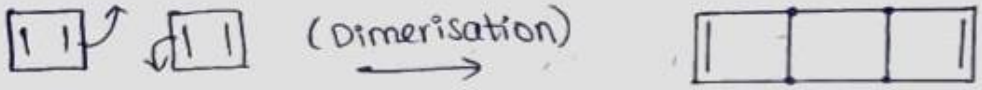
*) Note :

Benzyne undergoes dimerisation and trimerisation.



*) Note :

Anti-aromatic compounds undergo dimerisation



(AA) (AA)

$4\pi e^{\ominus}$ $4\pi e^{\ominus}$

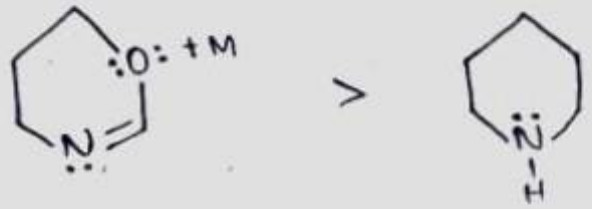
(Non-aromatic)

Basic strength :

* NH_3 > pyridine

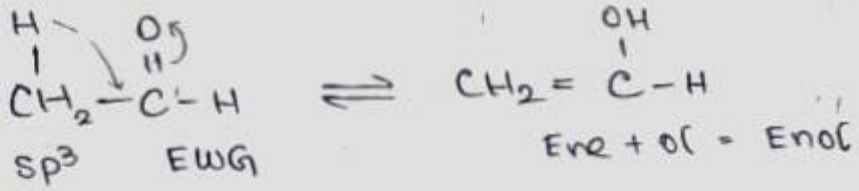
* Imidazole > pyridine

If Nitrogen or oxygen show "+M" to Nitrogen, its basic nature will be high.



*) Tautomerism ; (OR) Krylomerism (OR) Allelotropism (OR) Desmotropism (OR) Prototropy :

- This is one type of functional isomerism in which isomers are interchangeable or interconvertable and those isomers are in dynamic equilibrium with each other.



(Ethanal) (Acetaldehyde)
(Keto)

- In this isomerism, "H" atom is oscillating blw polyvalent atoms. When the hydrogen migrates there will be change in linkage or bond & position of π-bond changes.

*) Conditions for tautomerism :

i) Compound containing electronegative atom and bonded with multiple bond.

ii) There should be an acidic hydrogen atom present on sp^3 hybridised α-carbon.